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Contributions from the Chemical Laboratory of Harvard College.

CXXIII.—CERTAIN DERIVATIVES OF METADIBROMDINITROBENZOL.[1]

BY C. LORING JACKSON AND W. P. COHOE.

The dibromdinitrobenzol, melting at 117°.4, was made by Körner in his classical research on "Isomerism of the Aromatic Compounds with Six Atoms of Carbon,"[2] but its constitution has not been determined with certainty. Nietzki and Schedler,[3] in a recent paper, have proved that the dichlordinitrobenzol, melting at 103°, has the structure $Cl_21.3.(NO_2)_24.6$, and as this substance is made from the action of fuming nitric acid on metadichlorbenzol, just as the dibrom compound is made from metadibrombenzol, there is good reason to believe that they have the same constitution; but we thought it necessary to prove that this was the case before we studied this dibromdinitrobenzol further. For this purpose we heated the substance with aniline, and obtained the dianilidodinitrobenzol melting at 186°, which Nietzki and Schedler had obtained from their dichlordinitrobenzol; the dibrom substance therefore has the structure $Br_2 1.3.(NO_2)_2 4.6$. If aniline acted on the dibromdinitrobenzol in the cold, a bromanilidodinitrobenzol, $C_6H_2BrC_6H_5NH(NO_2)_2$, melting at 157°, was obtained, and this occurs in a yellow and in a red modification, which seem to differ in crystalline form as well as in color. This seems to be a case of dimorphism, as the two forms pass into each other with great ease. The yellow form is converted into the red by crystallization from benzol, the red into the yellow by heating to 135°. Similar phenomena have been observed in the cases of anilidotrinitrophenyltartronic ester[1] and trianilidodinitrobenzol.[2]

---

[1] Presented to the American Academy of Arts and Sciences, December 13, 1899.

[2] Gazz. chim. ital., 1874, 305.

[3] Ber. d. chem. Ges., 30, 1666 (1897).

After the constitution of the 1.3.4.6 dibromdinitrobenzol had been determined, we studied the action of sodic ethylate upon it, in the hope of encountering the replacement of bromine by hydrogen under the action of this reagent, which has been studied for some years in this laboratory. But no such behavior was observed; the action ran in the normal way, resulting in the formation of dinitroresorcindiethyl ether melting at 133°, discovered by Warren and one of us,[3] and proved to have the symmetrical structure by Koch and one of us;[4] so that this observation confirms the determination of the constitution of this body by the action with aniline.

Sodic phenylate converted the dibromnitrobenzol into diphenoxydinitrobenzol, which melts at 129°. The action of sodic malonic ester was tried on this compound to determine whether the phenoxy groups could be replaced by the malonic ester radical $CH(COOC_2H_5)_2$; as it has been found[5] that the best way to make dichlordimalonicesterquinone,

$$C_6Cl_2[CH(COOC_2H_5)_2]_2O_2,$$

is by treating dichlordiphenoxyquinone with sodic malonic ester, and we wished to see whether the nitro groups would produce the same effect as the oxygen atoms of the quinone in promoting the replacement of the phenoxy groups by malonic ester radicals. We found that phenol was eliminated when the diphenoxydinitrobenzol was treated with sodic malonic ester, and from the very unmanageable product a sodium salt was obtained which contained an amount of sodium corresponding to $C_6H_2OC_6H_5CNa(COOC_2H_5)_2(NO_2)_2$; so that we feel justified in assuming that the reaction has consisted in the replacement of the phenoxy by the malonic ester group.

---

[1] Jackson and Bentley: This JOURNAL, **14**, 348.

[2] Jackson and Herman: *Ibid.*, **16**, 37.

[3] *Ibid.*, **13**, 170.

[4] *Ibid.*, **21**, 510.

[5] Jackson and Grindley: *Ibid.*, **17**, 597.

The dibromdinitrobenzol, when reduced with zinc dust and acetic acid, gave a dibrommetaphenylenediamine, which was identical with that melting at 135° obtained by the action of bromine on metaphenylene diacetamide.[1] It follows from our preparation of this base that it has the constitution

$$Br_2 1.3.(NH_2)_2 4.6.$$

In all this work we have been careful not to approach too near to the field reserved by Nietzki and Schedler in their paper on dichlordinitrobenzol.

Preparation of Metadibromdinitrobenzol.

Monobromacetanilide was first made by passing a stream of air laden with the vapor of bromine through 5 liters of water in which 50 grams of acetanilide were suspended. The end of the reaction was determined by the appearance of a lasting yellow color in the liquid and a distinct change in the appearance of the solid. In all our attempts to convert this product into the dibromacetanilide by the action of liquid bromine on it when suspended in water, we observed the formation of a considerable amount of symmetrical tribromaniline,

$$(NH_2 1.Br_3 2.4.6.),$$

produced undoubtedly by the action of bromine on the free base proceeding from the saponification of some of the bromacetanilide by the hydrobromic acid formed in the reaction. The monobromacetanilide was accordingly filtered out, and, after being dried, suspended in glacial acetic acid or chloroform, to which a little more than the calculated amount of bromine was then added, drop by drop. This method gave an excellent yield of the dibromacetanilide with little trouble.

---

[1] Jackson and Calvert: This JOURNAL, 18, 482.

The dibromacetanilide was saponified by boiling it with sulphuric acid, of sp. gr. 1.44, in a flask with a return condenser, until the solution of the solid, which was usually accompanied by a darkening color, showed that the reaction was complete. The liquid was then allowed to cool, when most of the dibromaniline crystallized out, and what remained in solution was precipitated by the addition of a large quantity of water.

To remove the amido group, 100 grams of the dibromaniline were suspended in a mixture of 300 cc. of alcohol and 120 cc. of benzol, to which 20 cc. of sulphuric acid had been added; the mixture was heated in a flask on the steam-bath and 60 grams (a large excess) of solid sodic nitrite added as fast as the reaction would permit. The contents of the flask, which had taken on a reddish color, were boiled for an hour, and then allowed to stand over night, after which a large quantity of water was added, and the precipitated oily liquid distilled over with steam. A small amount of tribrombenzol is usually present, which appears as a solid in the condenser toward the end of the distillation with steam; it is well to stop the distillation as soon as this solid appears. The distillate with steam was dried with calcic chloride and distilled, and the fraction boiling from 210° to 225° collected for use. A small additional amount of dibrombenzol was obtained by extracting with ether the aqueous portion of the steam distillate, but the increase of the yield in this way was so small that this extraction was hardly worth while.

The dibrombenzol was converted into dinitrodibrombenzol by boiling it with fuming nitric acid, of sp. gr. 1.52, or better, a mixture of this acid and sulphuric acid. As soon as the oil had dissolved in the acid the reaction was complete; the boiling was stopped, and the product precipitated by pouring the acid liquid into a large quantity of cold water. The yellow crystals thus obtained were purified by crystallization from alcohol, until they showed the constant melting-point, 117°.

Determination of the Constitution of Metadibromdinitrobenzol by the Action of Aniline.

Two grams of the dibromdinitrobenzol, melting at 117°, were heated with an excess of aniline on the steam-bath for half an hour. At the end of this time the excess of aniline was removed by treatment with dilute hydrochloric acid, and the yellow residue, after being washed thoroughly with water, was recrystallized from a mixture of alcohol and benzol until it showed the constant melting-point 185°, which is essentially identical with 186°, that of the dianilidodinitrobenzol prepared from dichlordinitrobenzol by Nietzki and Schedler.[1] As they established the constitution $(NHC_6H_5)_2 1.3.(NO_2)_2 4.6$ for this body, the dibromdinitrobenzol, melting at 117°, must have the corresponding structure, $Br_2 1.3.(NO_2)_2 4.6$.

Action of Aniline on Symmetrical Dibromdinitrobenzol in the Cold: Bromanilidodinitrobenzol.

Two grams of the dibromdinitrobenzol, cooled by a freezing-mixture, were moistened with aniline, and the mixture was allowed to stand packed in ice for twelve to eighteen hours. The excess of aniline was then removed by dilute hydrochloric acid, and the dense yellow residue, after thorough washing with water, was purified by crystallization from alcohol and benzol until it showed the constant melting-point of 157°, when it was dried at 100° and analyzed with the following result:

I. 0.0994 gram substance gave, by the method of Carius, 0.0558 gram AgBr.

II. 0.2138 gram substance gave 0.1229 gram AgBr.

	Calculated for $C_6H_2BrC_6H_5NH(NO_2)_2$.	Found. I.	II.
Br	23.67	23.89	24.46

Properties of Bromanilidodinitrobenzol,
$C_6H_2BrC_6H_5NH(NO_2)_2$ $(Br1.C_6H_5NH3.(NO_2)_2 4.6.)$.

This substance crystallizes from a mixture of benzol and alcohol, sometimes in much modified short and thick flat prisms, apparently of the monoclinic system, resembling certain crystals of feldspar; at other times in rhombic plates, occasionally with some of the angles slightly beveled, which pass into forms like rhombohedra; all of these crystals have a full golden-yellow color. Other crystals were distinguished from these by their brilliant red color and by appearing in square prisms, modified on one of their angles or on two opposite angles. From these two colors, red and yellow, and the difference at least in crystalline habit, if not really in crystalline form, we infer that the substance appears in two closely related modifications. The yellow form, in which the substance is obtained from its preparation, becomes gradually converted into the red by crystallization from a mixture of alcohol and benzol, but several crystallizations are necessary to make this conversion complete. If, however, the yellow form is dissolved in benzol alone, the solution deposits, as it evaporates, a red oil, which, on stirring, solidifies to the red crystals. All the other common organic solvents, except the alcohols, also convert the yellow into the red form by a single crystallization. On the other hand, if the red crystals are heated in an air-bath, they begin to assume a yellow color at 110°, and are completely converted into the yellow form at 135°; this conversion is attended with no change in weight. The substance melts at 157°, forming a red liquid, which, when cooled and stirred, solidifies to the yellow modification. It is obvious that the melting-point given above is that of the yellow form, since the red is converted into the yellow at 135°. The bromanilidodinitrobenzol is freely soluble in benzol, soluble in toluol or chloroform, slightly soluble in ether, acetone, amyl alcohol, or hot ethyl alcohol. The best solvent for it is a mixture of benzol and alcohol.

---

[1] Ber. d. chem. Ges., **30**, 1668 (1897).

Determination of the Constitution of Metadibromdinitrobenzol by Treatment with Sodic Ethylate.

One gram of the dibromdinitrobenzol, melting at 117°, was mixed with an excess of sodic ethylate, prepared by the action of sodium on a considerable excess of absolute alcohol, and after the mixture had stood for some time at ordinary temperatures the excess of alcohol was allowed to evaporate spontaneously. The residue, after repeated washings with hot water, was purified by crystallization from a mixture of ligroin and benzol, when it was found to melt at 133°, the melting-point of the dinitroresorcinediethyl ether, discovered by Warren and one of us,[1] which it also resembled in crystalline form. As Koch and one of us[1] have proved that this dinitroresorcinediethyl ether has the constitution

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[1] This JOURNAL, 13, 170.

$$(OC_2H_5)_2 1.3.(NO_2)_2 4.6,$$

it follows that the dibromdinitrobenzol, melting at 117°, has the constitution $Br_2 1.3.(NO_2)_2 4.6$, a result which confirms that already obtained from the action of aniline.

Action of Sodic Phenylate with Symmetrical Dibromdinitrobenzol.

The sodic phenylate for this experiment was prepared by adding 5 grams of powdered sodic hydrate to enough melted phenol to make a pasty mass. While this was still in the viscous state, 5 grams of the dibromdinitrobenzol were added little by little with constant stirring, the beaker containing the mixture being kept cool with ice-water. The product, a dark-brown, solid mass, was treated with water, filtered, and the insoluble portion recrystallized either from slightly dilute alcohol or from a mixture of benzol with a large excess of ligroin, until it showed the constant melting-point 129°, when it was dried *in vacuo*, and analyzed with the following results:

I. 0.2494 gram substance gave, on combustion, 0.5563 gram CO_2 and 0.0903 gram H_2O.

II. 0.3746 gram substance gave, on combustion, 0.8457 gram CO_2. The water was unfortunately lost.

	Calculated for $C_6H_2(OC_6H_5)_2(NO_2)_2$.	Found.	
		I.	II.
C	61.38	60.82	61.59
H	3.41	4.02	....

The method of making sodic phenylate given above was adopted because in alcoholic solution the sodic phenylate gave principally the dinitroresorcindiethyl ether, and in aqueous solution there was no action until high temperatures were reached, and then the yield was unsatisfactory.

Properties of the Dinitroresorcindiphenyl Ether, $C_6H_2(OC_6H_5)_2(NO_2)_2$. $((OC_6H_5)_2 1.3.(NO_2)_2 4.6.)$.

This substance, when crystallized from a mixture of benzol and alcohol, forms slender white prisms terminated by one slanting plane, or, when better developed, by two planes meeting at a very obtuse angle and modified by several smaller ones, so that a blunt end is formed. It melts at 129°. It is freely soluble in benzol; soluble in cold toluol or chloroform, or in alcohol, ligroin, or acetone when these solvents are hot; slightly soluble in ether or amyl alcohol. The best solvent for it was either dilute alcohol or ligroin containing a little benzol.

---

[1] *Ibid.*, **21**, 510.

Some experiments were tried to determine whether the phenoxy groups in the diphenoxydinitrobenzol could be replaced by malonic ester radicals ($CH(COOC_2H_5)_2$), as a replacement of this sort had been observed in the case of dichlordiphenoxyquinone.[1] The solid diphenoxydinitrobenzol was dissolved in an alcoholic solution of sodic malonic ester, and the mixture allowed to stand at ordinary temperatures over night; afterward it was treated with dilute sulphuric acid, which precipitated an oil, and showed that phenol had been set free by the strong smell of this substance. The oily precipitate, after washing with water, was extracted with ether, which removed from it a pale-yellow oily substance; but as this did not solidify, even after standing for several months, we tried to determine its nature by the analysis of a salt. A specimen of the oil was dissolved in alcohol and treated with an aqueous solution of sodic hydrate, which threw down a bright-red precipitate; this was washed with benzol, dried *in vacuo*, and analyzed with the following results:

I. 0.1383 gram substance gave 0.0191 gram Na_2SO_4.
II. 0.1476 gram substance gave 0.0228 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_2OC_6H_5CNa(COOC_2H_5)_2$.	Found. I.	II.
Na	5.23	4.47	5.01

The results of these analyses, in connection with the elimination of phenol, prove that the reaction has run as was expected. The phenoxydinitrophenylmalonic ester separated from the salt as an oil, and therefore we did not think it worth while to attempt a more careful study of it.

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[1] Jackson and Grindley: This JOURNAL, **17**, 597.

Reduction of Symmetrical Dibromdinitrobenzol with Zinc Dust and Acetic Acid.

Twenty grams of zinc dust were placed in a flask fitted with a Bunsen valve and connected with a carbonic dioxide generator, acetic acid of 85 per cent was added, and then 5 grams of the dibromdinitrobenzol in small portions at a time, as under these conditions the reaction ran quietly and smoothly, although accompanied by blackening in every case. The reduction was carried on at first in the cold, but toward the end of the operation the mixture was heated gently on the steam-bath. After two hours the reaction was complete, when the insoluble portion was filtered out and extracted with dilute alcohol, which, upon cooling, deposited crystals melting even in the crude state at 131°. The filtrate from the insoluble reduction-products was treated with an excess of sodic hydrate sufficient to dissolve the zinc salts, the precipitate formed in this way filtered out and extracted with hot dilute alcohol, which gave another portion of the crude product melting at 131°. After purification, by crystallization from alcohol, the melting-point became constant at 134°; it was dried *in vacuo*, and analyzed with the following result:

0.1407 gram substance gave, by the method of Carius, 0.1976 gram of AgBr.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	59.78

This dibromphenylenediamine melts practically at the same point (135°) as that prepared by S. Calvert and one of us[1] from metaphenylenediacetamide and bromine. It also crystallizes like this in white needles, which turn brown on exposure to the air. As the constitution of our dibromdinitrobenzol is $Br_2 1.3.(NO_2)_2 4.6$, it follows that this dibrommetaphenylenediamine must have the corresponding constitution,

$$Br_2 1.3.(NH_2)_2 4.6.$$

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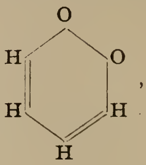
[1] This JOURNAL, 18, 482.

CXXIV.—ON CERTAIN DERIVATIVES OF ORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND WALDEMAR KOCH.

Attempts to prepare the orthobenzoquinone,



have been mentioned, so far as we can find, in only two papers. The first is that by Zincke,[2] in which he describes tetrabromorthoquinone and tetrachlororthoquinone, but says that a number of attempts to make the unsubstituted orthoquinone have failed to produce the desired result. The second is by Hinsberg and Himmelschein,[3] who obtained orthodioxydiphenylsulphone by the action of potassic dichromate on a mixture of pyrocatechin and benzolsulphinic acid, and draw the inference that the formation of this substance probably was preceded by the formation of orthoquinone. They add that all their experiments to isolate orthoquinone have failed because of its strong tendency to condensation and polymerization.

It seemed to us that one probable cause of the ill success of these experiments was the sensitiveness of the orthoquinone to oxidizing agents; this view was confirmed by the observations of Cousin,[4] that trichlorpyrocatechin and dibrompyrocatechin give only red resinous products with nitric acid, whereas the trichlor- or tribromhomopyrocatechin gives under the same conditions an orthoquinone; and also by some experiments undertaken by H. A. Torrey and one of us on the action of hydric dioxide or electrolytic oxygen on pyrocatechin, which led to unpromising black products. Accordingly, we searched for a method which would produce a quinone without the use of an oxidizing agent, and found one in the action of iodine on the lead salt of the dioxybenzol. After having shown that the method converted hydroquinone into quinone, we applied it to pyrocatechin ; but our first experiments led to no results, because we used alcohol as our solvent, which attacks the orthoquinone as soon as it is formed. Upon replacing the alcohol by chloroform we succeeded in obtaining a dark garnet-red solution, in which the presence of orthobenzoquinone was established by a number of tests given later in this paper.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Waldemar Koch. It was presented to the American Academy of Arts and Sciences May 9, 1900.

[2] Ber. d. chem. Ges., **20**, 1776 (1887).

[3] *Ibid.*, **29**, 2025 (1896).

[4] Ann. chim. phys., (7), **13**, 485.

From this solution we next tried to isolate the solid orthoquinone but, after trying every method we could devise, which gave even a remote promise of success, we have failed to obtain a trace of solid orthoquinone, and are forced to the opinion that it cannot exist in the solid state, or even for any length of time in solution. The products obtained in place of the orthoquinone in every case were a black substance insoluble in chloroform, and a brown substance, or mixture of substances, which dissolved in chloroform ; this brown product we have not attempted to investigate, but we have studied the black insoluble product and can give a fairly complete account of its nature in spite of its unsatisfactory properties. It begins to form in the chloroform solution of the orthoquinone in less than an hour, and is best obtained by allowing the solution to stand in a corked flask for not more than thirty hours. A combustion of the substance gave results corresponding to the formula $C_{12}H_8O_5$; the analysis of a lead salt prepared in a somewhat different way indicated the same formula, and this was confirmed by two analyses made by H. A. Torrey of his product from the electrolytic oxidation of pyrocatechin, which seemed to be identical with ours, and by an analysis of the benzoyl derivative of our black substance ; we have, therefore, five analyses of four different samples, all of which agree with each other, and leave no doubt that the substance is a definite compound and has the formula $C_{12}H_8O_5$. This formula indicates that the compound was formed by the union of 2 molecules of orthoquinone with the introduction of an additional hydroxyl group, a view which is confirmed by the analysis of the lead salt, $C_{12}H_6O_5Pb$, in which there are evidently two benzol rings to each atom of lead. When we consider the manner in which these two benzol rings are united, two theories seem especially worthy of attention; first, the two rings may be joined directly, so that the compound is a substituted diphenyl:

$$\text{(I)}\ O_2(HO)H_2C_6{-}C_6H_3(OH)_2\,;$$

or second, they may be united by 2 atoms of oxygen forming a substituted pyrocatechine ether according to this formula:

$$\text{(II)}\ (HO)H_3C_6{=}O_2{=}C_6H_2(OH)_2.$$[1]

The first (diphenyl) formula is rendered much more probable than the second by the analogy between our orthoquinone and the orthonaphthoquinone, which is converted by dilute sulphuric acid into dinaphthyldiquinhydrone,[2]

$$O_2H_5C_{10}{-}C_{10}H_5(OH)_2,$$

a black powder like our alteration-product; this has been proved by Korn[3] to be a dinaphthyl body by conversion into α-α-dinaphthyl and diphthalylic acid,

$$(COCO)(C_6H_4COOH)_2.$$

The support of the diphenyl formula by this analogy is so strong that we should feel it was hardly worth while to consider the second (ether) formula, if it were not for the fact that we have observed an oxygen attachment similar to that in Formula II in a derivative of tetrabromorthoquinone, described later in this paper. To decide between Formula I and Formula II we studied the action of reducing agents on the black substance, as, if it were an ether (Formula II), it should be reduced to a mixture of pyrocatechin and a trioxybenzol, whereas a diphenyl compound (Formula I) would only take up 2 atoms of hydrogen without decomposition.[4] We selected as the reducing agent sodium amalgam and water, because this had proved effective in breaking up the pyrocatechin ether containing bromine already alluded to; but, even after long-continued action on our black alteration-product, not a trace of pyrocatechin could be detected; the only reduction-product was a black substance evidently as complex as the original body. This result, therefore, declares decisively in favor of the diphenyl structure (Formula I).

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[1] In both these formulas the third hydroxyl group may be attached to the other benzol ring.

[2] Stenhouse and Groves: Ann. Chem. (Liebig), **194**, 205.

[3] Ber. d. chem. Ges., **17**, 3020.

[4] Korn did not succeed in splitting dinaphthyldiquinhydrone into simpler bodies by reduction. Ber. d. chem. Ges., **17**, 3024.

The action of benzoyl chloride on the black substance in presence of sodic hydrate converted it into a tribenzoyl derivative, $C_{12}H_5O_2O_3(COC_6H_5)_3$, thus proving the existence of three hydroxyl groups in the substance; and this benzoyl derivative, and also the original black compound, gave new substances with phenylhydrazine, which contained nitrogen, as was shown by the analyses. Unfortunately, the percentage of nitrogen found in both cases was far below that required by the probable formulas, which is undoubtedly accounted for by the difficulty in purifying these amorphous and infusible substances; our analyses, therefore, amount only to qualitative proofs of the presence of nitrogen. The introduction of the nitrogen, however, makes it highly probable that both the original substance and its tribenzoyl derivative contain oxygen atoms in the quinone position. We feel justified from the results of the foregoing experiments in assigning to the black alteration-product the formula

$$O_2(HO)H_2C_6—C_6H_3(OH)_2,$$

in which two of the hydroxyl groups are probably in the ortho position to each other, since the substance forms a stable lead salt when treated with plumbic acetate.

We have made no progress toward determining the position of the third hydroxyl group, which may even be attached to the other benzol ring. The introduction of this third hydroxyl group is not without analogy, since the dinaphthylorthoquinone, $C_{10}H_5O_2—C_{10}H_5O_2$, is converted by the action of the air on its solution in weak alkali into the dioxy compound, $C_{10}H_4OHO_2—C_{10}H_4OHO_2$.[1] In our case, however, the oxygen of the air took no essential part in the reaction, as the same alteration-product was formed in an atmosphere of carbonic dioxide; and this is not surprising, as we have had frequent occasion to observe that the orthobenzoquinone is a much stronger oxidizing agent than the orthonaphthoquinone, so that one portion of it might easily oxidize the other during the polymerization. The portions of the orthoquinone which gave up oxygen during the formation of the black body were undoubtedly converted into the brown substances soluble in chloroform, which made up about half of the total product.

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[1] Korn: Ber. d. chem. Ges., 17, 3021.

Although, as has been already stated, we could not obtain the orthoquinone in the solid state, many of its properties can be determined from the study of its solution in chloroform; thus, there can be little doubt that it has an intense red color and little, if any, odor, as the solution smelt of nothing but chloroform, whereas a smell as strong as that of paraquinone could have been detected even in presence of the amount of chloroform used. Its very slight stability has been dwelt on at sufficient length already, but we should add that it seems to be decomposed at once by even small quantities of water or alcohol.

We turn next to the reactions of the solution on which is based our inference that it contained orthoquinone. Hydrochloric acid converted it into monochlorpyrocatechin, which, however, was mixed with a little pyrocatechin, as would be expected, since Wichelhaus[1] has shown that the action of hydrochloric acid on parabenzoquinone consists in the formation of hydroquinone and chlorine, which subsequently react together, and in this corresponding case part of the pyrocatechin formed could well have escaped the substituting action of the chlorine. Reducing agents like ammonic sulphide or sulphurous dioxide produced pyrocatechin from this chloroform solution. Bromine formed with it tetrabrompyrocatechin, the reduction of the orthoquinone being achieved in this case by the hydrobromic acid formed in making the substituted quinone.

When the chloroform solution was added, drop by drop, to a solution of benzolsulphinic acid, also in chloroform, an orthodioxydiphenylsulphone, $C_6H_5SO_2C_6H_3(OH)_2$, melting at 153°, was formed, which should be identical with that obtained by

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[1] Ber. d. chem. Ges., **12**, 1504.

Hinsberg and Himmelschein[1] by oxidizing pyrocatechin in presence of benzolsulphinic acid, but the properties of the two substances show they are different. Hinsberg and Himmelschein's substance contained water of crystallization, and melted at 117°, if this were not driven off; at 143° to 145° after heating in the steam-bath; and at 164°, if completely dried by previous fusion; our compound contained no water, and melted at 153°, whether dried at ordinary temperatures or by previous melting. We have not succeeded in finding the conditions under which Hinsberg and Himmelschein's compound is formed, so that we were unable to compare the two substances, and must consider with our present knowledge that they are isomeric.

With aniline the chloroform solution gave a dianilidoquinoneanil, $C_6H_2(C_6H_5NH)_2O(C_6H_5N)$, which melted at 203°, and by this and a careful comparison of its other physical properties was proved to be identical with the body prepared by Zincke and von Hagen[2] from paraquinone by the action of aniline and acetic acid. As this substance has previously been made only from paraquinone, it has always been supposed that it contains the oxygen and anil group in the para position to each other, but after our preparation of it from orthoquinone it is also possible that it is a derivative of orthoquinone; and some weight is given to this view by the fact that it is formed easily from the orthoquinone by aniline alone, whereas it can be prepared from the paraquinone only with difficulty, and by the combined action of aniline and acetic acid. On the other hand, it seems hardly probable that a derivative of orthoquinone would be so stable as this; and the β-naphthoquinone forms with aniline and alcohol a corresponding anilidonaphthoquinoneanil,

$$C_{10}H_5O(C_6H_5NH)(C_6H_5N),$$

which is undoubtedly a derivative of α-naphthoquinone. Zincke[3] also has obtained recently from the azimidodichlororthoquinone by warming it with aniline an azimidoanilidomonochloroxyparaquinone, and similar cases of conversion of

[1] Ber. d. chem. Ges., **29**, 2025.

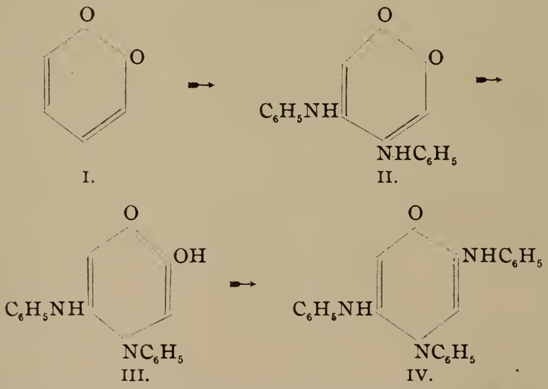
[2] *Ibid.*, **18**, 785.

[3] Ann. Chem. (Liebig), **311**, 276.

orthoquinones into derivatives of paraquinones are not rare. We are so strongly of the opinion, therefore, that our dianilidoquinoneanil is a para body with the constitution

$$O,1.C_6H_5N,4.(C_6H_5NH)_2,2.5,$$

that we have not thought it worth while to submit the question to an experimental investigation, which would, of necessity, require much time. Assuming that the constitution given above is correct, the body would be formed from the orthoquinone by the following series of transformations, which are modeled after those worked out by C. Liebermann[1] for the corresponding case of β-naphthoquinone :



The replacement of the two hydrogen atoms of the orthoquinone by the anilido groups to form II. takes place under the oxidizing influence of another portion of the orthoquinone, which takes up hydrogen to form pyrocatechin (always formed in our process) ; II. then passes by isomerization into III., which is converted into IV. by the further action of aniline.

Upon treating the solution of orthoquinone with orthophenylenediamine no phenazine was formed, but the reaction seemed to consist only in the oxidation of the diamine.

[1] Ber. d. chem. Ges., 14, 1664.

We have also devoted some attention to the study of the tetrabromorthoquinone, and have obtained from it two derivatives. The first of these was prepared by treating tetrabromorthoquinone with tetrabrompyrocatechin dissolved in acetic acid and water; it was a beautiful red body, which was soluble only in warm nitrobenzol. Its ormula was $C_{12}Br_6O_4$, and it was formed by the following reaction,

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_{12}Br_6O_4 + 2HBr,$$

as was shown by the detection of hydrobromic acid as one of the products of the reaction, and the fact that a good yield was obtained only when the two reagents were used in equal amounts. This formation of the substance is most naturally explained by supposing that the two benzol rings are united by two of the atoms of oxygen, forming a substituted pyrocatechin ether, $C_6Br_4{=}O_2{=}C_6Br_2O_2$, but it is also possible that the union took place directly between the two benzol rings forming a diphenyl compound with this formula, $O_2Br_3C_6{-}C_6Br_3O_2$, the 2 atoms of bromine removed in this reaction combining with the atoms of hydrogen of the pyrocatechin, and thus oxidizing it so that the body contains two orthoquinone groups. To decide between these two formulas the substance was submitted to reduction with sodium amalgam, as under these circumstances the pyrocatechin ether should be split into 2 molecules of pyrocatechin, while the diphenyl compound should be reduced without splitting the molecule. The principal product of this reduction was a chocolate-brown substance, which contained an amount of bromine nearly identical with that of the original body, and was converted into it again by nitric acid. With it there was always formed a certain amount of pyrocatechin, and this seemed to us strongly in favor of the ether formula, but it could not be considered conclusive, as the amount of pyrocatechin was much less than that of the brown product. In the hope of increasing the yield of pyrocatechin we submitted the brown product again to the action of sodium amalgam, but found it was entirely unaffected; we accordingly oxidized it to the original red body—a reaction which takes place quantitatively—reduced this again by sodium amalgam, obtaining fresh quantities of pyrocatechin and the brown body, and continued these alternate reductions and oxidations until the original specimen of the red body had been completely converted into pyrocatechin. Although we could wish that this conversion had taken place by reduction alone, the use of the oxidations cannot be held to vitiate the argument, as they gave a quantitative yield of the original substance, and we feel justified, therefore, in inferring that the two benzol rings are united by two atoms of oxygen, and that the substance is a pyrocatechin ether.

The brown product formed by the action of sodium amalgam was also obtained by the action of tribrompyrogallol on the tetrabromorthoquinone, and of hydrochloric acid at 160° to 175° on the red pyrocatechin ether. There seems no doubt, therefore, that it is formed from the red body by the conversion of two orthoquinone oxygen atoms into hydroxyl groups; in other words, that it is the pyrocatechin corresponding to the red orthoquinone; and this view is confirmed by the oxidation of the brown substance to the red by nitric acid. The reaction of the hydrochloric acid is especially instructive in regard to the constitution of these two bodies, as it is the familiar conversion of a quinone to a hydroquinone by this reagent. The red color of the original substance also points to the presence of orthoquinone oxygen in it, whereas the lighter color of the reduction-product (brown when crystallized, but purplish-white when amorphous) confirms the view that it is the hydroxy compound. We therefore assign the following formulas and names to these substances: red compound, $Br_4C_6{=}O_2{=}C_6Br_2O_2$, hexabromorthoquinopyrocatechin ether; the brown reduction-product, $Br_4C_6{=}O_2{=}C_6Br_2(OH)_2$, hexabromdiorthoxypyrocatechin ether. The only observed fact not in accordance with this last formula is that the substance does not dissolve in a solution of sodic hydrate, as we should expect it to do considering that it contains two phenol hydroxyls; this may, however, be explained by the very slight solubility of the substance (soluble only in warm nitrobenzol), which might prevent the solution of sodic hydrate from coming into sufficiently close contact with it to react.

The hexabromorthoquinopyrocatechin ether was formed when acetic acid or alcohol was used as the solvent, but none of it was obtained when the tetrabromorthoquinone and tetrabrompyrocatechin were mixed in solution in chloroform or ether. In this latter case the residue left after the evaporation of the solvent was a reddish white mass, apparently a mixture of the unaltered reagents, which contained none of the hexabromorthoquinopyrocatechin ether. This is strange, as Zincke, by mixing the two substances in ethereal solution, obtained a black crystalline substance. An attempt will be made in this laboratory next year to find the conditions under which this black compound is formed.

We have succeeded also in obtaining a reaction similar to that just described from tribromresorcin and tetrabromorthoquinone. The other phenols tried acted simply as reducing agents. The product proved to be a ditribrommetoxyphenyldibromorthoquinophenylene ether,

$$(C_6HBr_3OHO)_2C_6Br_2O_2.$$

This substance melts at 217°, and like the reduction-product just described, does not dissolve in a solution of sodic hydrate, in spite of the two phenol hydroxyl groups it contains, according to its most probable formula. We should explain this anomaly in the same way as before, although this substance is much more soluble than the reduction compound.

With glacial acetic acid the tetrabromorthoquinone, $C_6Br_4O_2$, formed a white compound, to which we have given much attention, but of which we can only give a very imperfect account. Zincke,[1] in his paper on tetrabromorthoquinone, noticed that it was attacked by glacial acetic acid, but did not isolate the product; on the other hand he obtained a white body by crystallizing tetrabromorthoquinone from ether and ligroin, which we have not succeeded in preparing. When tetrabromorthoquinone is evaporated to dryness with glacial acetic acid, a small amount of the red hexabromorthoquinopyrocatechin ether is formed, but the greater part of the quinone is converted into a white crystalline body melting at 230°, the analysis of which led to one of the two following formulas, $C_{14}H_2Br_8O_5$ or $C_{14}Br_8O_5$. The first would be formed by the union of 2 molecules of the tetrabromorthoquinone with 1 of acetic acid, 1 molecule of water being eliminated, thus:

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[1] Ber. d. chem. Ges., 20, 1777.

$$2C_6Br_4O_2 + C_2H_4O_2 = C_{14}H_2Br_8O_6 + H_2O.$$

The second would be formed from the first by removing 2 atoms of hydrogen, which could be done by the oxidizing action of another portion of the tetrabromorthoquinone, and the tetrabrompyrocatechin thus formed would then give rise to the red body, which always accompanied the white product; but the amount of this red compound always fell far below that which should be formed, if it had taken such an important part in the reaction (10 grams of tetrabromorthoquinone should give 5 grams of the red product, whereas the usual yield was only 0.8 gram), and, as the amount of hydrogen found in the white compound was distinctly larger than should have been given by a body free from that element, we have decided to adopt provisionally the formula $C_{14}H_2Br_8O_5$. We had hoped to settle this question by studying the decomposition-products of this substance, but so far it has either been unaffected or completely decomposed by all the reagents we have tried. We hope that in the coming year the study of this body will be completed and the work carried on in various other directions in this laboratory.

EXPERIMENTAL PART.

Action of Iodine on the Lead Salt of Hydroquinone.

These experiments were tried to test the efficacy of this method of making quinones. An aqueous solution of 10 grams of hydroquinone was treated with the calculated amount of sodic hydrate in a flask, to which the air had access only through a tube containing an alkaline solution of pyrogallol; to the sodium salt thus formed an aqueous solution of plumbic acetate was added, which gave a white precipitate of the lead salt. As this blackened rapidly on exposure to the air, no attempt was made to filter it, but an alcoholic solution of 5 grams of iodine was added directly to the precipitate suspended in the liquid, when plumbic iodide was formed, as shown by the appearance of a yellow color. After the reaction seemed to have come to an end, the insoluble substances were filtered out, and the filtrate, which had a strong odor of quinone, extracted with ether. This ether extract left, on evaporation, yellow crystals with a strong odor of quinone, which under the microscope showed the characteristic form of this substance, and after purification by sublimation melted at 112°–113°, which, although distinctly below the melting-point of quinone, 115°.7, is near enough to it to prove, in conjunction with the other properties, that quinone was formed.

To prove that this quinone was formed by the action of the iodine on the lead salt and not by the oxidizing effect of the air, a specimen of the salt mixed with water was exposed to the air for several hours, until it was thoroughly blackened; upon filtration a red solution was obtained which had no odor of quinone. Extraction with ether did not remove the red color, and on the evaporation of the ether, crystals of hydroquinone were obtained, recognized by the melting-point, but no quinone. Upon adding an alcoholic solution of iodine to a similar specimen of the lead salt blackened by exposure to the air, the sharp odor of quinone was observed at once, and a considerable amount of this body was obtained from the filtrate. The method, therefore, is applicable to the production of quinones, but naturally would be used only in cases where oxidation is inadmissible.

We also tried some experiments with iodine and the lead salt of resorcin, but as it was evident that the purification of the product would be a matter of great difficulty, we have postponed the continuation of this work until we have finished the study of pyrocatechin.

ORTHOQUINONE.

Action of Iodine on the Lead Salt of Pyrocatechin, Preparation of a Solution of Orthoquinone.

To prepare the lead salt of pyrocatechin 2 grams of pyrocatechin dissolved in 150 cc. of water were added gradually, with constant stirring, to a boiling solution of 7.5 grams of plumbic acetate in 250 cc. of water. The precipitated lead salt was allowed to settle, filtered out, and washed five times with hot water. It was then dried at 100° and finely pulverized. It is not advisable to use more than 2 grams of pyrocatechin at a time in making the lead salt, as with larger amounts it was found to be hard to wash out all the impurities.

Ten grams of this lead salt were thoroughly moistened with chloroform in a 500 cc. glass-stoppered flask. The salt must be absolutely dry, and the chloroform free from water and alcohol, as these substances decompose orthoquinone. A boiling solution of five grams of iodine in 200 cc. of chloroform was then added to the lead salt and the whole shaken well for five to ten minutes, after which, upon filtering through a dry Gooch crucible, a garnet-red solution of orthoquinone was obtained. The amount of iodine used in this experiment is a little more than half that required by the theory (1 molecule to each molecule of the lead salt). This large excess of the lead salt was used to avoid as far as possible the presence of iodine in the chloroform solution, and in this we were fairly successful, as a sample of it, when tested with a fresh specimen of the lead salt of pyrocatechin, showed only a trace of plumbic iodide.

This chloroform solution contained orthobenzoquinone, $C_6H_4O_2 1.2$, as is proved by the experiments described later in this paper, and it must have been a nearly pure solution of this body, since the only other substance which could have been present was iodine, and the amount of this was very small, as shown in the preceding paragraph. It had a dark garnet-red color, and no odor could be perceived except that of the chloroform. Within an hour from the time of its preparation it began to show signs of alteration by depositing a black precipitate, and after twenty-four to thirty hours all the orthoquinone had disappeared from the solution. We have made numerous attempts to isolate the solid quinone from its solution in chloroform, of which the following is a brief summary: Evaporation spontaneously at ordinary temperatures; evaporation at —12°; evaporation *in vacuo* of a solution in pure chloroform made from chloral, so as to avoid all traces of alcohol which decomposes the orthoquinone; evaporation by a stream of dry air or dry carbonic dioxide passed through the solution cooled by a freezing-mixture; precipitation with ligroin at —5°; precipitation with tetrachloride of carbon at —20°; we had great hopes of this last attempt, as we had not succeeded in making any of the orthoquinone, when tetrachloride of carbon was substituted for chloroform in the preparation, and we inferred from this that the quinone probably was insoluble in this substance; but this, as well as all the other experiments mentioned above, did not lead to the desired result. The product in every case was the black alteration-product already mentioned, the nature of which will be discussed presently, so that we are forced to the conclusion that the orthobenzoquinone cannot exist for any length of time, if at all, in the solid state.

STUDY OF THE ALTERATION-PRODUCT OF ORTHOBENZOQUINONE.

This substance was most conveniently obtained by allowing the chloroform solution of orthobenzoquinone, prepared as already described, to stand at ordinary temperatures in a corked flask from twenty-four to thirty hours.[1] The black precipitate thus formed was not easy to purify, for although it was soluble in alcohol and some other solvents, all our attempts to crystallize it have failed; we finally decided to depend for its purification on its insolubility in chloroform and benzol. Accordingly, after filtering it out from the chloroform in which it was formed, we washed it thoroughly with chloroform and afterward extracted it three times with hot benzol. About 40 per cent of the orthoquinone used was converted into this black product. In calculating this yield we assumed that the amount of orthoquinone in the chloroform solution corresponded to the amount of iodine used in making it. The black substance, after it had been purified by extraction with benzol, was dried *in vacuo* and analyzed with the following results:

0.2041 gram substance gave, on combustion, 0.4684 gram CO_2 and 0.0696 gram H_2O.

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[1] The solution should not be allowed to stand more than thirty hours, as in that case the product is contaminated with a brown impurity.

	Calculated for		
	$C_{12}H_6O_2(OH)_2$.	$C_{12}H_5O_2(OH)_3$.	Found.
C	66.67	62.07	62.59
H	3.70	3.45	3.79

These numbers would indicate that the substance has been formed by the union of 2 molecules of orthoquinone with the introduction of a hydroxyl group, but it is obvious that the composition of a body like this, which is amorphous and has no definite melting-point, can be determined only by the analysis of several samples prepared by different methods. Accordingly, we undertook the preparation and analysis of the lead salt, which should be insoluble and stable, if the substance contains two hydroxyls in the ortho position to each other, as would be the case if it is formed from 2 molecules of orthoquinone. Further, as we thought that the additional hydroxyl indicated by the analysis might have been introduced by the action of the oxygen of the air, we repeated the preparation in an atmosphere of carbonic dioxide. The solution of orthoquinone was made from the lead salt of pyrocatechin and iodine in a flask filled with this gas, and was separated from the plumbic iodide by means of a rose filter with an asbestos film without exposing it to the air. Upon standing over night, still in an atmosphere of carbonic dioxide, a black precipitate was formed, identical in appearance with that obtained by the ordinary process. This was purified in the way already described, and then converted into its lead salt as follows: 0.3 gram of this black body dissolved in 40 cc. of alcohol was added to a boiling solution of 1 gram of plumbic acetate in 400 cc. of water; this large amount of water is necessary to prevent the alcohol from precipitating plumbic acetate, which, becoming imprisoned in the lead salt, could hardly be removed by washing. The jet-black lead salt thus obtained was washed five times with hot water, dried at 100°, and analyzed with the following result:

0.2352 gram of the salt gave 0.1645 gram $PbSO_4$.

	Calculated for		
	$C_{12}H_6O_2O_2Pb$.	$C_{12}H_5O_2OHO_2Pb$.	Found.
Pb	49.17	47.39	47.76

This result shows that the oxidizing agent, which introduces the additional hydroxyl, is not the oxygen of the air, but the orthoquinone itself, and this view is confirmed by the fact that the chloroform solution, from which the black compound has separated, contains brown substances probably formed from the orthoquinone in oxidizing the insoluble product, but which were so unmanageable that we were unable to determine their composition.

We would add here two analyses made by H. A. Torrey some years ago in this laboratory of a substance agreeing with our black compound in its properties, which he had prepared by the electrolytic oxidation of pyrocatechin. They gave the following results :

I. 0.1275 gram substance gave, on combustion, 0.2940 gram CO_2 and 0.0436 gram H_2O.

II. 0.0608 gram substance gave 0.1401 gram CO_2 and 0.0230 gram H_2O.

	Calculated for $C_{12}H_5O_2(OH)_3$.	Found.	
		I.	II.
C	62.07	62.88	62.85
H	3.45	3.80	4.20

The substance is obviously the same as that previously analyzed, although not so pure.

We have, therefore, four analyses of three samples of this substance prepared or purified in different ways, and, as these agree, there can be no doubt that the black alteration-product of the orthoquinone is a definite compound, and has the composition $C_{12}H_8O_5$.

Properties of the Black Alteration-Product of Orthobenzoquinone (*Orthodioxyphenyloxyorthoquinone*,[1] $C_6H_3(OH)_2C_6H_2(OH)O_2$).– It forms an almost black amorphous powder, which does not melt, but decomposes gradually at temperatures above 170°. It is easily soluble in cold alcohol, ether, or glacial acetic acid ; insoluble in benzol or chloroform, whether cold or hot. Strong acids have no apparent action on it, but alkalies dissolve it.

The following experiments were undertaken to determine the constitution of the black alteration-product.

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[1] This name and formula for the substance are established by the work described later in this paper.

Reduction of the Alteration-Product.

The formula of the substance $C_{12}H_8O_5$ indicates that it contains two benzol rings, and these may either be united directly, forming a diphenyl compound, or they may be united by 2 atoms of oxygen, forming a substituted pyrocatechin ether $[C_6H_3OH]O_2[C_6H_2(OH)_2]$. The diphenyl formula, $(HO)O_2H_2C_6—C_6H_3(OH_2)$, is rendered probable by the formation of the dinaphthyldiquinhydrone[1] under somewhat similar circumstances from β-naphthoquinone, which has been proved to be a dinaphthyl compound;[2] the pyrocatechin-ether formula, on the other hand, is in harmony with a derivative of tetrabromorthoquinone, which is described later in this paper. Reduction seemed the easiest way to decide between these formulas, as the ether should be split into pyrocatechin and a trioxybenzol, while the diphenyl product would be reduced without splitting apart the two benzol rings. Upon treating the black alteration-product with sodium amalgam and water in an atmosphere of carbonic dioxide for several days, an uninviting black solid was obtained on acidification, which was soaked in water, and this water, as well as the acidified filtrate from the reduction extracted with ether, but not a trace of pyrocatechin was obtained. As the bromether, which we have obtained in another part of our work, gives a large quantity of pyrocatechin by this treatment, we infer that the black alteration-product is a diphenyl derivative.

Action of Benzoyl Chloride on the Black Alteration-Product.

Half a gram of this substance was dissolved in 10 cc. of a solution of potassic hydrate (1 : 5), and to the warm solution benzoyl chloride was added drop by drop, until the product of the reaction rose to the surface as an oily mass, leaving the liquid clear. This was then treated with sodic hydrate, in which it did not dissolve, and thoroughly washed with water. The tarry mass thus obtained was dissolved in chloroform, the solution filtered, and the filtrate mixed with an excess of alcohol, which precipitated out the substance. After drying *in vacuo* it was analyzed, with the following result :

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[1] Ann. Chem. (Liebig), **194**, 205.

[2] *Ibid.*, **206** ; Korn : Ber. d. chem. Ges., **17**, 3020.

0.2210 gram substance gave, on combustion, 0.5933 gram CO_2 and 0.0744[1] gram H_2O.

	Calculated for		
	$C_{12}H_6O_3(OCOC_6H_5)_2$.	$C_{12}H_5O_2(OCOC_6H_5)_3$.	Found.
C	70.91	72.79	73.21
H	3.64	3.68	3.74

The substance is therefore a tribenzoyl compound, and the original black body must have contained three hydroxyl groups. This *benzoxyorthoquinoorthodibenzoxydiphenyl*,

$$C_6H_2(OCOC_6H_5)O_2C_6H_3(OCOC_6H_5)_2,$$ [2]

forms a light-yellow, amorphous powder without a definite melting-point. It is easily soluble in chloroform; insoluble in alcohol or water. Alkalies do not dissolve it.

The fact that only three benzoyl groups are taken up by the black alteration-product indicates that two of its five atoms of oxygen do not form part of hydroxyl groups; from the formation of the substance these two atoms of oxygen must either belong to a quinone or be the connecting atoms of a pyrocatechin ether, and, as our work on the reduction of the alteration-product has shown that it is probable they are not pyrocatechin-ether oxygen atoms, there can be little doubt that they occur in the quinone configuration, which indeed was the more probable supposition of the two. We tried to confirm this inference by the formation of hydrazones both from the original black alteration-product and its benzoyl derivative, but without satisfactory results. When phenylhydrazine in excess was added to a solution of 0.5 gram of the black alteration body dissolved in 10 cc. of alcohol, the dark, blackish color of the solution was discharged, and on pouring the product into acidified water a golden-yellow precipitate was formed; but an analysis of the substance gave 6.39 per cent of nitrogen, whereas the most probable formula, $C_{12}H_8O_4NNHC_6H_5$, requires 8.70 per cent of nitrogen. The tribenzoyl derivative of the black substance was dissolved in chloroform and boiled with an excess of phenylhydrazine for several minutes; a new compound was formed, which was obtained by allowing the chloroform to evaporate spontaneously, treating with an acid to remove the excess of phenylhydrazine, dissolving the residue in cold alcohol, and precipitating the substance from this solution with water. After drying *in vacuo* it was analyzed and 3.19 per cent of nitrogen found instead of 4.42 per cent of nitrogen required by the formula of the hydrazone,

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[1] A little water was lost in this analysis.

[2] The distribution of the benzoxy groups in this substance has not been determined.

$$C_{12}H_5O(NNHC_6H_5)(OCOC_6H_5)_3.$$

It is evident from these results that phenylhydrazine acts on both of these substances, and that the product in each case contains nitrogen. The results, therefore, as far as they go, confirm our inference that there are two quinone atoms of oxygen in the black substance, but they are of little value, because the exceedingly unmanageable nature of both of these substances prevented us from purifying them sufficiently to determine their composition with certainty.

The work just described establishes the following points with tolerable certainty. The black alteration-product is a diphenyl compound and contains three hydroxyl groups and an orthoquinone group; it may therefore be called orthodioxyphenyloxyorthoquinone, and receive the formula

$$C_6H_3(OH)_2C_6H_2(OH)O_2,$$

although the three hydroxyl groups may be attached to the same benzol ring, as we have not determined the position of the third hydroxyl experimentally.

EXPERIMENTS WITH THE SOLUTION OF ORTHOBENZOQUINONE.

Action of Hydrochloric Acid on the Solution of Orthobenzoquinone.

Dry hydrochloric acid gas was passed through a fresh chloroform solution of orthoquinone (prepared from iodine and the lead salt of pyrocatechin) until it fumed strongly. After filtering out a slight tarry precipitate, a large part of the chloroform was recovered by distillation, and the concentrated solution thus obtained allowed to stand over night in an open vessel. The residue, which was usually oily, was heated on the steam-bath to drive off the last traces of the solvent and a slight impurity of iodine, and then extracted with a hot mixture of 3 parts chloroform with 1 of ligroin, which left behind a large quantity of a black oil. The solution became milky, on standing, and deposited an oily substance, followed, when it had cooled, by the formation of crystals. As soon as these crystals began to appear the clear solution was decanted from the oil and allowed to crystallize in a separate vessel. The residual oils, by a similar treatment with chloroform and ligroin, yielded an additional amount of the crystals. The crystals were dissolved in benzol and treated with bone-black, after which they were purified by repeated crystallizations from the mixture of chloroform and ligroin. They showed the melting-point 84° to 85°, which was not quite constant, indicating that the substance was not perfectly pure; but in spite of this it was dried *in vacuo*, and analyzed with the following result:

0.2005 gram substance gave, by the method of Carius, 0.1865 gram of AgCl.

	Calculated for $C_6H_3Cl(OH)_2$.	Found.
Cl	24.57	23.00

This result indicates that the body is monochlorpyrocatechin, but that it contains some pyrocatechin, as would be expected if the reaction ran in the same way as that of hydrochloric acid on parabenzoquinone, since Wichelhaus[1] has shown that in this case hydroquinone and chlorine are formed in the first instance, and that the substitution compounds, which form the final product, are made by the action of the chlorine on the hydroquinone. We have not attempted to purify the chlorpyrocatechin more thoroughly, as much time and labor would be necessary to obtain sufficient material for this purpose, and the formation of chlorpyrocatechin under these conditions is confirmed by the following analysis of the lead salt, made by adding plumbic acetate to an aqueous solution of the product of the reaction of hydrochloric acid on the solution of orthoquinone.

0.3867 gram salt gave 0.3306 gram of plumbic sulphate.

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[1] Ber. d. chem. Ges., **12**, 1504.

	Calculated for $C_6H_3ClO_2Pb$.	Found.
Pb	58.98	58.55

The monochlorpyrocatechin in the slightly impure state in which we obtained it crystallized in white pearly plates, which are easily soluble in water, alcohol, ether, benzol, chloroform, or acetone; insoluble in ligroin. With an aqueous solution of plumbic acetate it gives a lead salt. It blackens quickly if exposed to the air after treatment with an alkali. The melting-point observed by us is, of course, of no value on account of the presence of the impurity of pyrocatechin.

Behavior of the Solution of Orthobenzoquinone with Reducing Agents.

Ammonic Sulphide.—Some of the solution of orthoquinone in chloroform was shaken with about one-third of its volume of the ordinary laboratory solution of ammonic sulphide. The red color of the orthoquinone disappeared, and the aqueous solution took on a dark color. The two liquids were separated by means of a drop funnel, and the chloroform was extracted twice with water, the extracts being added to the ammonic sulphide solution at first obtained. The mixed aqueous portion was then heated on the steam-bath, acidified with hydrochloric acid, allowed to stand until the precipitated sulphur had settled, filtered, and the clear, dark-colored filtrate extracted with ether. The residue, left on the evaporation of the ether, was recrystallized twice from benzol, when it was found to melt constant at 103° to 104°, and to show all the other properties of pyrocatechin. In order to be certain that the pyrocatechin, detected in the product from the action of ammonic sulphide on the orthoquinone solution, was formed from the orthoquinone, it was necessary to prove that this solution contained no free pyrocatechin; for this purpose a small amount of it, taken before the reduction, was shaken with water, the water evaporated, and the residue extracted with benzol; the benzol extract was evaporated to dryness, the very slight residue dissolved in water, and tested with plumbic acetate, when it gave no precipitate, showing that no free pyrocatechin was contained in the chloroform solution.

Action of Sulphurous Dioxide.—Dry sulphurous dioxide was passed through the chloroform solution of orthoquinone until it was saturated; the principal product was a black unmanageable precipitate, probably a compound of orthoquinone and pyrocatechin corresponding to quinhydrone; but the filtrate from this left, on evaporation, crystals which were recognized as pyrocatechin by their properties and the formation of the lead salt.

Action of Bromine on the Solution of Orthobenzoquinone.

An excess of bromine was added to the solution of orthoquinone in chloroform, the chloroform allowed to evaporate spontaneously, and the crystalline residue, after being heated gently to drive off the excess of bromine, was spread on unglazed porcelain to remove oily impurities. After recrystallization from benzol it showed the constant melting-point 191°, which is near enough to 192° to 193°, that given by Zincke[1] for tetrabrompyrocatechin, to leave no doubt as to the nature of the substance. For greater certainty the substance was analyzed with the following results:

I. 0.1835 gram substance gave, by the method of Carius, 0.3210 gram AgBr.

II. 0.1509 gram substance gave 0.2637 gram AgBr.

	Calculated for $C_6Br_4(OH)_2$.	Found. I.	II.
Br	75.11	74.44	74.39

These numbers are sufficiently near to show that the product of the action of bromine on the orthobenzoquinone is tetrabrompyrocatechin.

Behavior of the Solution of Orthobenzoquinone with Benzolsulphinic Acid.

The chloroform solution of orthoquinone was added drop by drop to a solution of benzolsulphinic acid,[2] also in chloroform, until the color began to disappear less rapidly and the solution of the sulphinic acid had assumed a decided reddish tint.

[1] Ber. d. chem. Ges., 20, 1777.

[2] If the conditions were reversed, and the solution of benzolsulphinic acid was added to the solution of orthoquinone, none of the desired sulphone was obtained; we ascribe this difference in behavior to the oxidation of the sulphinic acid by the excess of orthoquinone.

After standing over night the liquid was filtered, the filtrate evaporated to dryness, and the residue allowed to solidify. The solid residue was next treated with hot benzol, which dissolved all but a slight black residue. On allowing the benzol solution to evaporate, a crystalline substance was obtained, which was purified by crystallization with the aid of boneblack at first from water mixed with a little alcohol, finally from water alone, until it showed the constant melting-point 153°, when it was dried at 100° and analyzed with the following results:

I. 0.2353 gram substance gave, on combustion, 0.4931 gram CO_2 and 0.0862 gram H_2O.

II. 0.1454 gram substance gave, by the method of Carius, 0.1418 gram BaSO4.

	Calculated for $C_6H_3(OH_2)SO_2C_6H_5$.	Found.	
		I.	II.
C	57.60	57.14	....
H	4.00	4.07	....
S	12.80	....	13.39

As this body must be a substituted pyrocatechin it should give a lead salt, and upon trying it with a solution of plumbic acetate we obtained one, which was analyzed with the following result:

0.2601 gram substance gave 0.1729 gram PbSO4.

	Calculated for $C_6H_3O_2PbSO_2C_6H_5$.	Found.
Pb	45.50	45.39

There can be no doubt, therefore, that the substance is a pyrocatechinsulphone or orthodioxydiphenylsulphone.

Properties of Orthodioxydiphenylsulphone, $C_6H_3(OH)_2SO_2C_6H_5$.—It crystallizes from alcohol and water in short, thick, well-formed, white prisms terminated by two planes at an obtuse angle to each other. It contains no water of crystallization and melts at 153°. It is easily soluble in alcohol, ether, chloroform, or glacial acetic acid; very slightly soluble in cold water or benzol, freely soluble in either of these liquids when hot; essentially insoluble in ligroin, either hot or cold. Alkalies dissolve it with a yellow color. Ferric chloride gives a bluish-green color with it, which changes to red on the addition of sodic carbonate. As has been already mentioned, its aqueous solution gives a precipitate with plumbic acetate.

This substance has the same composition as the orthodioxydiphenylsulphone made by Hinsberg and Himmelschein[1] by oxidizing pyrocatechin in presence of benzolsulphinic acid, and we should expect that the two bodies would be identical, but, strangely enough, they seem to be isomers, since Hinsberg and Himmelschein's compound contains water of crystallization and melts in presence of this at 117°; when dried in the steam-oven, at 143° to 145°; when previously fused in the air, at 164°; whereas, our substance contains no water, and melts at 153°, whether dried at ordinary temperatures or by previous fusion. We made five attempts to prepare their compound according to Hinsberg and Himmelschein, but did not succeed in finding the conditions under which it is formed, which must lie within very narrow limits; and, as in doing this we had devoted more time to the subject than we could afford, we were obliged to abandon our intention of making a comparative study of the two compounds.

Action of Aniline on the Solution of Orthobenzoquinone.

The solution of orthoquinone in chloroform was heated with an excess of aniline for five minutes on the steam-bath; the chloroform was then allowed to evaporate, and the residue, after having been freed from aniline by treatment with hydrochloric acid and washing with water, was purified by recrystallization from a mixture of two parts of alcohol to one of benzol, until it showed the constant melting-point 203°, when it was dried at 100° and analyzed with the following result:

0.2909 gram substance gave 28.2 cc. N at 22° and 774 mm.

	Calculated for $C_6H_2(C_6H_5NH)_2C_6H_5NO$.	Found.
N	11.51	11.27

The substance is therefore a dianilinoquinoneanil. When the aqueous wash-waters obtained in the preparation of this substance were extracted with ether pyrocatechin was obtained, recognized by its odor and lead salt.

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[1] Ber. d. chem. Ges., 29, 2025.

Properties of the Dianilinoquinoneanil, $C_6H_2(C_6H_5NH)_2C_6H_5NO$.—Crystallized from alcohol and benzol it forms bronze-colored small needles, melting at 203°, although they begin to draw together somewhat at 198°. The melting-point of this substance is identical with that (202° to 203°) given by Zincke and Hagen[1] for the dianilinoquinoneanil made from paraquinone by the action of aniline and glacial acetic acid, and as a comparison of the two substances showed they crystallized in the same form, there can be no doubt of their identity. The formation of a paraquinone derivative from our orthoquinone has been already explained in the introduction to this paper.

In the hope of obtaining a phenazine the solution of orthoquinone was treated with orthophenylenediamine; a reaction took place, the principal products of which consisted of uninviting black substances and pyrocatechin recognized by the formation of its lead salt. From the appearance of the pyrocatechin we inferred that the reaction consisted principally in the oxidation of the diamine by the orthoquinone, and as, even after trying the experiment under several varying conditions, no more promising results were obtained this line of work was abandoned. Phenol also gave, with the solution of orthoquinone, such an uninviting product that we did not attempt to study it. Sodic hydrate gives, with the orthoquinone solution, a green coloration similar to that obtained by the action of sodic hydrate on tetrabromorthoquinone.

DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.

The tetrabromorthoquinone used in this work was prepared as follows: 20 grams of pyrocatechin were dissolved in 50 cc. of glacial acetic acid and 37 cc. of bromine added gradually from a burette. The mixture was allowed to stand over night, after which the product was purified by recrystallization from 200 cc. of glacial acetic acid. In this way 40 grams of pyrocatechin yielded 118 to 126 grams of recrystallized tetrabrompyrocatechin; that is, between 75 and 80 per cent of the theoretical yield. To convert this tetrabrompyrocatechin into tetrabromorthoquinone 30 grams of it were dissolved in 300 cc. of glacial acetic acid by heating on the water-bath; the solution was then cooled to 16°, or until the glacial acetic acid began to solidify, and 11 grams of fuming nitric acid (sp. gr. 1.5) diluted with 60 cc. of glacial acetic acid added rapidly, the mixture being kept cool and stirred vigorously during the addition; after standing for five minutes 300 cc. of water were added and stirred in thoroughly. If the process had run successfully, the tetrabromorthoquinone settled to the bottom in a glistening mass of dark-red crystals, which were filtered off and dried. The product thus obtained melted at 145° to 147° instead of 150° to 151°, but was pure enough for our work, which was fortunate, as recrystallization from glacial acetic acid is attended by a great loss of material. Thirty grams of tetrabrompyrocatechin gave 18 grams of tetrabromorthoquinone, which amounts to about 60 per cent of the theoretical yield.

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[1] Ber. d. chem. Ges., 18, 787.

As has just been stated, the crystallization of tetrabromorthobenzoquinone from glacial acetic acid cannot be effected without considerable loss, which we found was due to the conversion of the tetrabromorthoquinone into two new bodies, one of which was red, the other white.[1] A more careful study of the conditions under which the red body was formed showed us that it was produced by the action of the orthoquinone with tetrabrompyrocatechin, either existing as an impurity in our tetrabromorthoquinone or formed from it by reduction. After this the study of this red product was carried on with comparatively little difficulty.

Preparation of Hexabromorthoquinopyrocatechin Ether, $C_{12}Br_6O_4$.

Eleven grams of tetrabromorthoquinone and 10 grams of tetrabrompyrocatechin were dissolved in 470 cc. of glacial acetic acid by heating the mixture on the steam-bath; 180 cc. of water were then added, which produced no immediate precipitate, and the mixture allowed to stand in a warm place for twenty-four hours. During this time a red precipitate was formed, which was filtered out and washed with hot alcohol to remove unaltered tetrabromorthoquinone and pyrocatechin. In this way 10.7 grams were obtained; that is, somewhat over 60 per cent of the theoretical yield. The purification of the substance offered at first some difficulty because it was insoluble in all the common solvents, but later we found that it dissolved to a limited extent in hot nitrobenzol, and proceeded as follows: Two grams of the crude red body were dissolved in 150 cc. of nitrobenzol by heating the mixture on the steam-bath (at higher temperatures more of the substance will dissolve, but the solution is attended with decomposition). Upon cooling, the solution deposited about 0.7 gram of crystals, which were submitted to a second similar crystallization from nitrobenzol at 100°, after which the product was extracted several times with hot alcohol to remove adhering nitrobenzol, dried at 100°, and analyzed. As the substance does not melt, we had no means of determining whether this treatment had been an efficient purification.

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[1] Zincke (Ber. d. chem. Ges., 20, 1777) observed that acetic acid acted on tetrabromorthoquinone but did not isolate the products of the action.

I. 0.1809 gram substance gave, on combustion, 0.1374 gram CO_2 and 0.038 gram H_2O.

II. 0.1008 gram substance gave, by the method of Carius, 0.1637 gram AgBr.

III. 0.1129 gram substance gave 0.1843 gram AgBr.

	Calculated for $C_{12}Br_6O_4$.	Found. I.	II.	III.
C	20.93	20.71	....	....
H	0.00	0.23	....	....
Br	69.76	....	69.13	69.49

Properties of Hexabromorthoquinopyrocatechin Ether.—The substance crystallizes from warm nitrobenzol in short, slender prisms of a pure vermilion-red color; it does not melt and is insoluble in all the common solvents; nitrobenzol dissolves it especially when warm, but if the solution is heated above 100° decomposition sets in, as shown by a change of color. The ordinary strong acids have no effect on it in the cold, but fuming nitric acid dissolves it with decomposition; alkalies do not dissolve it, but the substance turns black after standing with an alkali for a short time. The red color of the substance indicates that it contains two orthoquinone oxygen atoms, and this view is confirmed by its behavior with hydrochloric acid and reducing agents described later.

The red substance is probably formed from tetrabrompyrocatechin and tetrabromorthoquinone by the following reaction:

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_6Br_4O_2C_6Br_2O_2 + 2HBr.$$

To test this a new preparation was made as described above, and after the mixture had stood twenty-four hours it was diluted with five times its volume of water, the reddish-white precipitate formed filtered out, the aqueous filtrate acidified with nitric acid, and treated with argentic nitrate, when a heavy precipitate of argentic bromide was thrown down, showing the presence of hydrobromic acid among the products of the reaction. It was also found that the best yield was obtained when the two reagents were used in the proportion of equal molecules, as required by the reaction. The best solvent to be used in the preparation was glacial acetic acid and water, as already described, but the red body was also formed in dilute alcohol (the proportions used were 0.5 gram of each reagent, 40 cc. of alcohol, and 10 cc. of water). On the other hand, no reaction was observed when the solvent was ether or chloroform. One gram of each of the reagents was dissolved in 50 cc. of ether (care was taken that the substances were free from even a trace of acetic acid), and allowed to stand twenty-four hours. As no precipitate had formed, the ether was allowed to evaporate spontaneously, when a reddish-white residue was left, which looked like a mixture of the unaltered reagents, and dissolved completely in hot chloroform. This showed that none of the hexabromorthoquinopyrocatechin ether had been formed, as it is insoluble in chloroform. Another portion of the residue from the ethereal solution was dissolved in glacial acetic acid and slightly diluted, when a copious deposit of the red body appeared on standing. The fact that we observed no action when the tetrabromorthoquinone and tetrabrompyrocatechin were mixed in ether is strange, since Zincke[1] states that by the action of these two bodies in ether or benzol he obtained black shining needles, which changed color at 110° and formed a brownish liquid. We are unable to explain this difference in the results of the experiments, but hope that future work may lead us to the conditions necessary for preparing the black substance.

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[1] Ber. d. chem. Ges., 20, 1778.

If the substance is formed by the reaction given above, it is probable that the two benzol rings are connected by two of the atoms of oxygen ; but this is not necessarily the case, as the product might also be a derivative of diphenyl, in which both rings contain orthoquinone groups. To settle the mode of union of the two benzol rings, we submitted the substance to reduction with sodium amalgam, as follows: Ten grams of the red substance were covered with water in a flask, from which all the air was excluded by a stream of carbonic dioxide, 3 per cent sodium amalgam was then added in large excess, and the reaction was allowed to run at ordinary temperatures in the atmosphere of carbonic dioxide for several days. At the end of this time the red substance had been converted principally into a purplish-white body, which seemed to resist the further action of the sodium amalgam ; it was, therefore, filtered out and washed with dilute acid and alcohol ; the aqueous filtrate from this substance gave no precipitate on acidification, but on subsequent extraction with ether we obtained from the extract a considerable quantity of a white residue, which, after several crystallizations from benzol, gave the melting-point 100° instead of 104°, the true melting-point of pyrocatechin ; from the form of its crystals, however, and as it gave the lead salt and the characteristic color with ferric chloride, there can be no doubt that it was pyrocatechin. As has been stated, the principal product of this reduction was the purplish-white insoluble substance, the weight of which amounted to 6 grams from 10 grams of the red body ; it was obvious, therefore, that no safe inference in regard to the constitution of the red substance could be drawn from the appearance of this small proportion of pyrocatechin. Accordingly, in the hope of increasing our yield of pyrocatechin, this purplish-white product was submitted to reduction with sodium amalgam under the conditions used in its formation, the action in this case being allowed to continue for a week, but, as we had reason to expect from our observations in our first reduction, the substance remained essentially unaltered, not more than a trace of pyrocatechin being formed. Meanwhile, we had discovered that the purplish-white product was converted by nitric acid into the original red substance, and, therefore, we oxidized the unaltered body from the last reduction, and on reducing this again with sodium amalgam, obtained a fresh amount of pyrocatechin with the purplish-white product again. By repeating these alternate oxidations and reductions we have succeeded in converting a sample of the red substance completely into pyrocatechin, a result which, it seems to us, proves that this red body is a pyrocatechin ether and not a diphenyl derivative.

The purplish-white product of the reduction of hexabromorthoquinopyrocatechin ether by sodium amalgam, mentioned frequently in the preceding paragraph, proved to have the same solubilities as the mother substance; that is, it was insoluble in all the common solvents except nitrobenzol. It was accordingly recrystallized three times from boiling nitrobenzol, when, as it does not have a definite melting-point, it was assumed to be pure. After extraction with alcohol, to remove adhering nitrobenzol, it was dried at 100° and analyzed with the following result:

0.1215 gram substance gave, by the method of Carius, 0.1974 gram AgBr.

	Calculated for $C_{12}Br_6(OH)_2O_2$.	Found.
Br	69.56	69.16

Properties.—The substance crystallizes from hot nitrobenzol in very small chocolate-brown crystals, which appear to be short, rather blunt, needles. As obtained from reduction, it has a purplish-white color and a characteristic silky luster. It does not melt at 300°. It is insoluble in all the common solvents except nitrobenzol. An aqueous solution of sodic hydrate does not dissolve it; fuming nitric acid converts it back into the red substance from which it was made, as is proved by the following experiment:

Three grams of the chocolate-colored crystals of the reduction-product were mixed with 20 cc. of glacial acetic acid, and 5 cc. of fuming nitric acid were added. The solid immediately turned red, and, after the mixture had been thoroughly stirred, it was poured into water and washed. The oxidation was then repeated in the same way, and the dried product was found to weigh 3 grams; the conversion from the chocolate-colored substance to the red body, therefore, takes place quantitatively. The red product was recrystallized from warm nitrobenzol, freed from the excess of nitrobenzol with alcohol, dried at 100°, and analyzed with the following result:

0.1317 gram substance gave, by the method of Carius, 0.2140 gram AgBr.

	Calculated for $C_{12}Br_6O_4$.	Found.
Br	69.76	69.15

There can be no doubt that this substance is the hexabromorthoquinopyrocatechin ether described above.

As to the formula of the chocolate-colored product of the reduction there is a certain amount of doubt. Our analysis shows only that its composition does not differ to a marked extent from that of the red mother-substance. Its formation by reduction and its conversion to the original body by nitric acid would indicate that it was the hydroxyl compound corresponding to the red quinone, but, on the other hand, its insolubility in sodic hydrate is hard to reconcile with this view. As this may be due, however, to the very slight solubility of the substance in all solvents, which might prevent the sodic hydrate from coming sufficiently in contact with it to react, we are inclined to consider that it is the hexabromorthodioxypyrocatechin ether, and to assign it provisionally the formula $C_{12}Br_6O_2(OH)_2$. We hope that the study of this substance may be finished in this laboratory in the near future.

Our attempts to decompose the hexabromorthoquinopyrocatechin ether with sulphuric acid led to no result, as no action was observed even after boiling it for several hours with sulphuric acid of 1.44 or even 1.6 sp. gr.; but hydrochloric acid reacted upon it, as is shown by the following experiment: 5 grams of the red body were sealed in a tube with 25 cc. of strong hydrochloric acid and heated from 160° to 175° for five hours; the product, after being washed with water and alcohol, showed a strong resemblance to the purplish-white body obtained by the reduction with sodium amalgam. On treating it with fuming nitric acid diluted with glacial acetic acid it turned red at once, so that there can be little doubt of the identity of the two substances. This observation can be satisfactorily explained on the theory already adopted, that the purplish-white substance is the dihydroxy derivative from the red orthoquinone body, as then this action is the familiar reduction of quinone oxygen by hydrochloric acid. This theory is still further supported by the reduction of tetrabromorthoquinone to the purplish-white body by tribrompyrogallol described in the next section.

Behavior of Tetrabromorthoquinone with Tribromresorcin.

After we had found, as just described, that tetrabromorthoquinone reacted with tetrabrompyrocatechin, it became of interest to try the action of the tetrabromorthoquinone with other diatomic phenols, and, as we found that unsubstituted phenols of this class reduced the quinone,—pyrocatechin, for instance, reducing it completely to tetrabrompyrocatechin,—we turned our attention to the bromphenols. Of these, tetrabromhydroquinone in alcoholic solution acted only as a reducing agent, giving bromanil and tetrabrompyrocatechin. Tribrompyrogallol also acted only as a reducing agent, giving tetrabrompyrocatechin, which combined with unreduced tetrabromorthoquinone to give the hexabromorthoquinopyrocatechin ether, and this was converted by further action of the tribrompyrogallol into its purplish-white reduction-product. With tribromresorcin, on the other hand, a new compound was obtained.

Eight and four-tenths grams of tetrabromorthoquinone and 7 grams[1] of tribromresorcin[2] were dissolved with the aid of heat in 600 cc. of glacial acetic acid mixed with 400 cc. of water, and allowed to stand for twenty-four hours. At the end of this time a dingy pink precipitate had formed, which was filtered out, washed, and recrystallized from benzol until it showed the constant melting-point 217°, when it was dried at 100°, and analyzed with the following result:

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[1] The two reagents were used in the proportion of equal molecules, whereas the analysis of the product showed that 2 molecules of the resorcin should have been taken for each molecule of the quinone.

[2] The tribromresorcin was prepared by the method of Benedikt (Monatsh. f. Chem., 4, 227) by mixing the calculated amount of bromine with resorcin dissolved in glacial acetic acid. The product was purified by crystallization from benzol and ligroin.

I. 0.1389 gram substance gave, by the method of Carius, 0.2173 gram AgBr.

II. 0.1370 gram substance gave, by the method of Carius, 0.2144 gram AgBr.

	Calculated for $(C_6Br_3HOHO)_2C_6Br_2O_2$.	Found. I.	II.
Br	66.94	66.58	66.61

The substance, therefore, is evidently formed by the union of 2 molecules of the resorcin with 1 of the quinone with elimination of 2 molecules of hydrobromic acid, and may be called the ditribrommetoxyphenyldibromorthoquinophenylene ether.

Properties.—It crystallizes from benzol in slender lemon-yellow prisms with square ends and melts at 217°. It is soluble in ether, slightly soluble in cold alcohol or chloroform, easily soluble in either of these solvents when hot; nearly insoluble in cold benzol, much more soluble in hot benzol, which is the best solvent for it. It does not dissolve in sodic hydrate, which throws some doubt on the formula we have ascribed to it, as this contains two hydroxyl groups.

Action of Glacial Acetic Acid on the Tetrabromorthoquinone.

As has been already stated, tetrabromorthoquinone, when crystallized from glacial acetic acid, is partially converted into a white substance,[1] which we found it convenient to prepare as follows: 10 grams of tetrabromorthoquinone were dissolved in 80 cc. of glacial acetic acid and the solution slowly evaporated to dryness on the steam-bath, the reddish-white residue was moistened with 10 cc. glacial acetic acid and the slow evaporation on the steam-bath repeated, in order to act on any tetrabromorthoquinone which might have escaped the previous reaction ; the residue was then extracted with 200 cc. of hot alcohol and filtered boiling, when the red hexabromorthoquinopyrocatechin ether previously described was left behind, as it is insoluble in alcohol. This substance seemed to be a constant product of the reaction, but not a principal one, as the amount was only about 0.8 gram. The alcoholic solution was allowed to cool and filtered again ; then it was diluted with 200 cc. of water, which precipitated out the white product, amounting to from 5 to 6 grams. This was purified by crystallization from glacial acetic acid until it showed the constant melting-point 230°, when it was dried at 100°, and analyzed with the following results :

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[1] Zincke (Ber. d. chem. Ges., 20, 1777) converted tetrabromorthoquinone, into a white substance by crystallizing it from a mixture of ether and ligroin. On repeating the experiment we did not succeed in finding the conditions under which the white product is formed.

I. 0.2658 gram substance gave, on combustion, 0.1903 gram CO_2 and 0.0179 gram H_2O.

II. 0.1373 gram substance gave, by the method of Carius, 0.2306 gram AgBr.

III. 0.3015 gram substance gave, on combustion, 0.2090 gram CO_2 and 0.0223 gram H_2O.

IV. 0.1265 gram substance gave 0.2122 gram AgBr.

V. 0.1279 gram substance gave 0.2147 gram AgBr.

VI. 0.1138 gram substance gave 0.1911 gram AgBr.

VII. 0.1229 gram substance gave 0.2074 gram AgBr.

	Found.						
	I.	II.	III.	IV.	V.	VI.	VII.
C	19.53	....	18.90	....	....	....	....
H	0.75	....	0.82	....	....	....	....
Br	....	71.45	....	71.39	71.44	71.48	71.83

Of these analyses I and II were of samples prepared and purified as described ; III to VII were of specimens prepared earlier in our work, and in some cases purified by slightly different, and perhaps less effective, methods.

Two determinations of the molecular weight were made by the method of freezing, the solvent being benzol.

I. 0.262 gram substance dissolved in 16.58 grams benzol produced a depression of 0°.099.

II. 0.594 gram substance in 16.58 grams benzol produced a depression of 0°.219.

	I.	II.
Molecular weight	782	802

The most probable formula to be derived from these data is $C_{14}H_2Br_8O_5$, formed by the union of 2 molecules of tetrabromorthoquinone with 1 of acetic acid, 1 molecule of water being eliminated. The results, however, agree almost as well with $C_{14}Br_8O_5$, although the percentage of hydrogen found is high for a substance which is free from this element. A compound with the formula $C_{14}Br_8O_5$ would be formed by the removal of 2 atoms of hydrogen from the preceding compound, a reaction which might easily be brought about by the oxidizing action of a portion of the tetrabromorthoquinone; the tetrabrompyrocatechin thus formed in turn acting on the unaltered quinone would give the red body which, as already stated, is always produced with the white substance; but it should be remembered that the quantity of the red body formed is far below that which would be expected from such a reaction.

	Calculated for		Found.	
	$C_{14}H_2Br_8O_5$.	$C_{14}Br_8O_5$.	I.	II.
C	18.88	18.92	19.53	....
H	0.22	....	0.75	....
Br	71.95	72.07	....	71.45
Mol. wt.	890	888	782	802

It is obvious that the decision can be made between these formulas only by the chemical study of the substance, but, unfortunately, we have not succeeded as yet in decomposing it by any of the reagents we have tried, so that we must leave this question undecided for the present, with the statement that we consider the formula $C_{14}H_2Br_8O_5$ the most probable. The study of the substance will be continued in this laboratory next year.

Properties of the Substance, $C_{14}H_2Br_8O_5$.—When crystallized from glacial acetic acid it forms small, almost square rhombic plates with a pearly luster, which melt at 230°. It is easily soluble in ether, benzol, chloroform, acetone, or ethyl acetate; almost insoluble in glacial acetic acid, but its solubility is increased by heat, as the boiling acid takes up from 2 to 3 per cent of the substance. Its solubility in ethyl alcohol is similar to that in glacial acetic acid; curiously enough, when first formed, the crude mass is rather freely soluble in alcohol, but, as the purification continues, it becomes less and less so, until, when pure, it is nearly insoluble in cold alcohol, as already stated. It is essentially insoluble in ligroin or in water, hot or cold. The best solvent for it is glacial acetic acid. None of the strong acids dissolve it when cold ; nor does even a hot solution of sodic hydrate show any perceptible action upon it.

The substance is decidedly stable, as is shown by the following experiments, which were tried in the hope of decomposing it into simpler bodies, in order to throw some light on its nature : 0.5 gram of the white substance were treated with sodium amalgam and water in an atmosphere of carbonic dioxide for eight days. At the end of this time the substance was recovered unaltered, as shown by its melting-point. The filtrate was acidified and extracted with ether, but yielded no pyrocatechin. Two-tenths gram of the substance was dissolved in boiling glacial acetic acid and mixed with 5 cc. of fuming nitric acid also diluted with glacial acetic acid ; no visible reaction took place, and upon dilution with water the original substance was obtained, as shown by the melting-point. Two-tenths gram was dissolved in cold chloroform and 3 cc. of bromine added ; after standing for twenty-four hours the chloroform was evaporated, leaving the original substance, as shown by the melting-point. Two-tenths gram of the substance was dissolved in benzol and an excess of aniline added ; after standing for twenty-four hours the benzol and aniline were removed, when the unaltered substance was obtained, as shown by the melting-point. Phenylhydrazine gave a similar negative result. No action could be observed when the substance was treated with an alkaline solution of potassic permanganate, or was boiled with sulphuric acid of sp. gr. 1.44 or 1.6, or heated to 150° in a sealed tube with hydrochloric acid. If it was heated to 250° with hydrochloric acid the compound was completely destroyed, and complete destruction also ensued when it was treated with fuming nitric acid, or a solution of chromic anhydride, or when it was fused with potassic hydrate. In continuing this work next year, renewed attempts will be made to obtain decomposition-products of the substance, and efforts will also be made to throw light on its constitution by preparing allied compounds.

It should also be mentioned that acetic ester converts tetrabromorthoquinone into tetrabrompyrocatechin, which then forms hexabromorthoquinopyrocatechin ether with unaltered tetrabromorthoquinone. Chloral showed no action with tetrabromorthoquinone even at 100°. The study of the little-known and very reactive tetrabromorthoquinone will be continued in various directions in this laboratory.

CXXV.—ON THE ACTION OF SODIC SULPHITE ON TRIBROMDINITROBENZOL AND TRIBROMTRINITROBENZOL.[1]

By C. Loring Jackson and Richard B. Earle.

In the course of an extended study of the action of various reagents on tribromdinitrobenzol ($Br_3 1.3.5.(NO_2)_2 2.4.$), it became of interest to determine whether this substance could be converted into a sulphonic acid by the method of Strecker,[2] that is, boiling the halogen compound with an aqueous solution of normal sodic sulphite, and experiments in this direction were tried rather early in the work, with negative results. Upon returning to the subject later we did not find any conditions under which an aqueous solution of sodic sulphite acted on tribromdinitrobenzol, but when we substituted alcohol for water as the solvent we obtained a reaction. This, however, took a different direction from that which we had expected, as under these conditions the sodic sulphite acts as a reducing agent, converting the tribromdinitrobenzol into dibromdinitrobenzol by replacing one of the atoms of bromine by hydrogen. The atom of bromine replaced is the one between the two nitro groups, since the dibromdinitrobenzol formed melted at 117°, which is the melting-point of the dibromdinitrobenzol,[3] $Br_2 1.3.(NO_2)_2 4.6$. That the product had this constitution was confirmed by its conversion into the bromanilidodinitrobenzol, which showed the melting-point 157°.[4] Tribromtrinitrobenzol undergoes a similar reduction with an alcoholic solution of normal sodic sulphite, the product being dibromtrinitrobenzol, which can have only this constitution: $Br_2 1.3.(NO_2)_3 2.4.6$. It is a new substance and melts at 135°.

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[1] Presented to the American Academy of Arts and Sciences, May 9, 1900.

[2] Ann. Chem. (Liebig), **148**, 90.

[3] Koerner : Gazz. chim. ital., 1874, 305.

[4] Jackson and Cohoe : This Journal, **26**, 5.

In the hope of finding an easier method for making this dibromtrinitrobenzol the action of dibromdinitrobenzol ($Br_2 1.3.(NO_2)_2 4.6$) with nitric and sulphuric acids was studied. This gave the desired dibromtrinitrobenzol, but the product was mixed with so large a proportion of tribromdinitrobenzol that the method was not adapted to the preparation of the substance. This tribromdinitrobenzol is a new substance melting at 150°. There can be no doubt that its constitution is $Br_3 1.2.3.(NO_2)_2 4.6$, since it is made by introducing a third atom of bromine into the dibromdinitrobenzol, $Br_2 1.3.(NO_2)_2 4.6$, and, if this occupied the only other vacant place (5), the product would be the common tribromdinitrobenzol, which melts at 192°. The formation of this tribromdinitrobenzol during this reaction is strictly according to the analogy of the behavior of the tribromdinitrobenzol, which, when boiled with a mixture of fuming nitric and sulphuric acids, gives rise to tribromtrinitrobenzol and tetrabromdinitrobenzol.[1]

As neither of the new substances just described can be prepared easily on a large scale, we have confined our work on them to the study of the principal action of sodic ethylate on each. This reaction runs in a normal way, giving styphnic diethyl ether,

$$C_6H(NO_2)_3(OC_2H_5)_2,\ ((OC_2H_5)_2 1.3.(NO_2)_3 2.4.6.),$$

with dibromtrinitrobenzol, recognized by its melting-point 121°; and with tribromdinitrobenzol a new bromdinitroresorcinmonoethyl ether melting at 78°. The subject did not promise to be of sufficient interest to make it worth while to study the secondary products of these reactions.

EXPERIMENTAL PART.

Action of Sodic Sulphite in Alcoholic Solution on Tribromdinitrobenzol.

Five grams of symmetrical tribromdinitrobenzol ($Br_3 1.3.5$

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[1] Jackson and Wing: This JOURNAL, 10, 284.

$(NO_2)_2 2.4$) were dissolved in 70 cc. of alcohol mixed with 20 cc. of benzol, 5 grams of normal sodic sulphite added, and the mixture boiled for five hours in a flask with a return condenser. The red liquid thus obtained was filtered from the insoluble portion, evaporated to dryness, and the residue washed with water, until the yellow color was removed. The part insoluble in water was then recrystallized from alcohol with the aid of bone-black, until it showed the constant melting-point 117°. This melting-point indicated that it was Koerner's dibromdinitrobenzol[1] ($Br_2 1.3.(NO_2)_2 4.6.$), and this was confirmed by treating it with aniline in the cold, when it was converted into the bromanilidodinitrobenzol,[2]

$$C_6H_2Br(C_6H_5NH)(NO_2)_2,$$

recognized by its melting-point 157°. For greater certainty the dibromdinitrobenzol was dried at 100° and analyzed with the following results :

I. 0.3277 gram substance gave 24.6 cc. N at 18°.5 and 760.3 mm.

II. 0.3195 gram substance gave, by the method of Carius, 0.3707 gram AgBr.

	Calculated for $C_6H_2Br_2(NO_2)_2$.	Found. I.	II.
N	8.59	8.65	....
Br	49.38	....	49.08

The sodic sulphite, therefore has removed the atom of bromine standing between the two nitro groups in the tribromdinitrobenzol and replaced it by hydrogen.

That this was not the only action of the sodic sulphite was shown by the marked yellow color of the products of the reaction. The yellow substance was soluble in water, but, in spite of its strong color, was present in such small quantity that we could not isolate it from the other substances soluble in water, which consisted of sodic bromide and unaltered sodic sulphite. It was undoubtedly the sodium salt of a phenol formed by a secondary reaction.

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[1] Gazz. chim. ital., 1874, 305.

[2] Jackson and Cohoe : This JOURNAL, **26**, 5.

Action of Sodic Sulphite in Alcoholic Solution on Tribromtrinitrobenzol.

Ten grams of symmetrical tribromtrinitrobenzol ($Br_3$1.3.5.$(NO_2)_3$2.4.6) were dissolved in 120 cc. of common alcohol with the assistance of 30 cc. of benzol, 10 grams of normal sodic sulphite added, and the mixture boiled for four hours in a flask fitted with a return condenser. The reaction seemed to run as in the case of the tribromdinitrobenzol, except that it took place more easily, since the red color appeared more quickly. The red solution was filtered, the filtrate evaporated to dryness, and the residue washed with water, after which it was recrystallized from a mixture of alcohol and benzol with the assistance of bone-black, until it showed the constant melting-point 135°, when it was dried at 100° and analyzed with the following results :

I. 0.2384 gram substance gave 25.1 cc. N at 25° and 753.3 mm.

II. 0.2887 gram substance gave, by the method of Carius, 0.2910 gram AgBr.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found. I.	II.
N	11.36	11.65	....
Br	43.10	....	42.89

The substance is, therefore, dibromtrinitrobenzol ($Br_2$1.3.$(NO_2)_3$2.4.6), formed by the replacement of 1 atom of bromine in the tribromtrinitrobenzol by hydrogen, and the sodic sulphite has behaved like a reducing agent in this case just as it did with the tribromdinitrobenzol.

Properties of Metadibrom-s-trinitrobenzol.—It crystallizes from benzol—or better, a mixture of benzol and ligroin—in broad prisms terminated by two planes at a slightly acute angle to each other, or in slender, blunt-ended prisms, or in rhombic crystals. It has a pale-yellow color with a slight greenish tinge, and melts at 135°. It is freely soluble in benzol or ether ; soluble in chloroform, acetone, or cold alcohol ; freely soluble in hot alcohol ; slightly soluble in hot ligroin ; insoluble in water. The best solvent for it is a mixture of alcohol and benzol, or of benzol and ligroin ; strong hydrochloric or sulphuric acid has no action on it, either hot or cold. Strong nitric acid does not dissolve it in the cold, but forms a yellow solution with it when hot, which deposits the unaltered substance on cooling. Sodic hydrate solution gives a pale yellow solution when hot; no perceptible action when cold. Alcoholic sodic hydrate gives a deep red color.

The aqueous wash-waters obtained in the preparation of dibromtrinitrobenzol by this process, although showing a strong red color, contained so little organic matter that we did not succeed in isolating any new compound from them. The residue left on evaporating them consisted chiefly of sodic bromide and unaltered sodic sulphite.

Preparation of Dibromtrinitrobenzol from Dibromdinitrobenzol.

In the hope of finding an easier method of preparing the dibromtrinitrobenzol we next tried to make it from dibromdinitrobenzol. The dibromdinitrobenzol was made by the method of Jackson and Cohoe,[1] which, however, we modified somewhat in converting the bromacetanilide into dibromacetanilide—the monobromacetanilide was mixed with enough glacial acetic acid to convert it into a semi-liquid mass, to which the calculated amount of bromine was added from a burette. It was then warmed on the steam-bath until it was transformed into a clear, dark-red liquid, which was poured into water, filtered, and the precipitate ground in a mortar with a solution of sodic hydrate to remove the excess of bromine. The dibromdinitrobenzol used for our work was recrystallized until it showed the correct melting-point 117°.

To convert the dibromdinitrobenzol into dibromtrinitrobenzol we proceeded as follows: Twenty grams of dibromdinitrobenzol were added to 500 cc. of fuming nitric acid of sp. gr. 1.50 and 200 cc. of sulphuric acid of sp. gr. 1.86, and the mixture was boiled violently for about three hours in a flask closed with a porcelain crucible. Toward the close of the operation a reddish oil separated, after which the process was continued only so long as the liquid boiled freely, since decomposition and darkening of the color resulted from too long-continued boiling. After the mixture had been boiled for a sufficiently long time it was allowed to cool, poured into ice-water, and filtered.

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[1] This JOURNAL, 26, 1.

The precipitate was recrystallized from a mixture of alcohol and benzol until it showed a constant melting-point, but as this stood at 150° the substance was not the expected dibromtrinitrobenzol, which melts at 135°. On examining the mother-liquors from this substance, however, we found the dibromtrinitrobenzol, which, after purification by crystallization from a mixture of benzol and ligroin, was recognized by its melting-point 135°, and the following analysis of the substance dried at 100°:

0.2174 gram substance gave, by the method of Carius, 0.2203 gram AgBr.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found.
Br	43.10	43.10

The dibromtrinitrobenzol is therefore formed by this process, but so much of the other product melting at 150° is formed at the same time that this is not a convenient method of preparing it, and the dibromtrinitrobenzol remains a not easily accessible substance.

Tribromdinitrobenzol,

$C_6HBr_3(NO_2)_2$, $(Br_3 1.2.3.(NO_2)_2 4.6.)$.

The substance melting at 150°, prepared by the action of nitric acid and sulphuric acid on dibromdinitrobenzol as described in the preceding section, was dried at 100° and analyzed with the following results:

I. 0.2973 gram substance gave, according to the method of Carius, 0.4138 gram AgBr.

II. 0.2987 gram substance gave 0.4150 gram AgBr.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found. I.	Found. II.
Br	59.26	59.24	59.13

The substance is, therefore, a tribromdinitrobenzol, and its appearance is not unexpected, since J. F. Wing and one of us[1] found that tetrabromdinitrobenzol was always formed during the preparation of tribromtrinitrobenzol from tribromdinitrobenzol. There can be no doubt about the constitution of this tribromdinitrobenzol, because it is made from the dibromdinitrobenzol ($Br_2$1.3.$(NO_2)_2$4.6) by the introduction of an atom of bromine which can enter only in two places—between the nitro groups or between the atoms of bromine. If the substitution takes place between the nitro groups there must be formed symmetrical tribromdinitrobenzol, which melts at 192°; there is left, therefore, for our substance melting at 150° only the constitution $Br_3$1.2.3.$(NO_2)_2$4.6.

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[1] This JOURNAL, 10, 284.

Properties of the 1.2.3. Tribrom-4.6. Dinitrobenzol.—Yellowish-white rectangular plates beveled on the sides, when crystallized from a mixture of alcohol and benzol. Melting-point 150°. It is freely soluble in benzol or ether; soluble in chloroform, glacial acetic acid, or acetone; soluble in cold alcohol, freely soluble in hot alcohol; slightly soluble in cold ligroin, soluble in hot; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong hydrochloric or sulphuric acid gives no visible action hot or cold. Strong nitric acid appears not to act in the cold, but dissolves it when hot, depositing the unaltered substance as it cools. A solution of sodic hydrate does not act on it apparently either hot or cold, but in presence of alcohol gives a light yellow color.

Action of Sodic Ethylate on Dibromtrinitrobenzol.

One and a half grams of dibromtrinitrobenzol ($Br_2$1.3.$(NO_2)_3$2.4.6) were dissolved in 15 cc. of benzol and mixed with sodic ethylate in the proportion of 3 molecules of the ethylate to each molecule of the dibrom compound. The sodic ethylate was prepared by adding the calculated amount of sodium to 30 cc. of absolute alcohol. The liquid at once took on an intense red color and became turbid. To make sure of completing the reaction the mixture was allowed to stand for twelve hours at ordinary temperature in a corked flask, after which it was filtered and the filtrate allowed to evaporate spontaneously; the residue was washed with water until the washings were colorless, and then recrystallized from alcohol until it showed a constant melting-point, which was found to be 121°. The melting-point of styphnic ethyl ether,

$$C_6H(OC_2H_5)_2(NO_2)_3 \quad (OC_2H_5)_2 1.3.(NO_2)_3 2.4.6,$$

is given as 120°.5, and it is described as forming long plates, which quickly turn orange-brown in the light ; our substance crystallized in prisms connected by their longer sides, and turned brown by exposure to the light. It contained no bromine. There can be no doubt, therefore, that the two bodies are identical, and that this styphnic ether formed by replacing each bromine by an ethoxy group is the principal product of the reaction. It was not, however, the only product of the action of sodic ethylate on dibromtrinitrobenzol, as the reaction product insoluble in the organic solvents, but soluble in water, gave tests for nitrite as well as bromide, and the aqueous washings were colored ; but the amount of these secondary products was so small that they could not have been studied without preparing the mother-substance on a very large scale, and the subject did not seem to be of sufficient importance to warrant the great expenditure of time which would have been necessary for this purpose.

Action of Sodic Ethylate on Adjacent Tribromdinitrobenzol.

Seven grams of the tribromdinitrobenzol ($Br_3 1.2.3.(NO_2)_2 4.6$) were dissolved in 70 cc. of benzol and mixed with sodic ethylate in the proportion of 3 molecules of the ethylate to each molecule of the tribromdinitrobenzol. The sodic ethylate was prepared by adding the calculated amount of sodium to 70 cc. of absolute alcohol. A deep-red turbid solution was formed immediately, which was allowed to stand in a corked flask at ordinary temperatures for two days, and then filtered, the filtrate allowed to evaporate spontaneously, and the residue washed with water until the washings were colorless. The portion insoluble in water after recrystallization from alcohol showed the constant melting-point 58°, and crystallized in long, white needles, turning yellow in sunlight, but was formed in such small quantity that there was not enough for analysis ; we, therefore, sought the principal product of the reaction in the portion soluble in water. The precipitate formed during the action of the sodic ethylate was dissolved in water and mixed with the wash-waters, which had previously been concentrated to a convenient bulk. The solution was then acidified with acetic acid, which threw down a black, tarry precipitate. This was filtered out, washed, suspended in water, and dissolved by adding sodic hydrate to neutralization; the solution was filtered and treated with baric chloride, which produced at once a mass of shining, yellow needles. These were filtered out, washed with water, and recrystallized several times from alcohol, after which they were dried at 100° and analyzed with the following results:

I. 0.3636 gram substance gave 0.1108 gram $BaSO_4$.

II. 0.3071 gram substance gave 21.2 cc. N at 22°.5 and 765 mm. The substance was mixed with a large excess of a mixture of 8 parts of fused plumbic chromate with 1 of potassic dichromate. It was necessary to heat very gradually to avoid too rapid an evolution of the nitrogen.

	Calculated for $[C_6HBr(NO_2)_2(OC_2H_5)O]_2Ba$.	Found. I.	 II.
Ba	18.33	17.91	....
N	7.47	....	7.86

The substance is, therefore, the barium salt of a bromdinitroethoxyphenol. We have not determined the constitution of this substance experimentally, but there can be little doubt that it is a derivative of resorcin, as the two bromine atoms in the meta position to each other are also in the para and ortho positions to the nitro groups, and this has been shown to be the position most favorable to replacement; whereas, the third atom of bromine, which is in the meta position to the two nitro groups, would be replaced with difficulty according to all previous work on this subject; we have no hesitation, therefore, in calling this substance the bromdinitromonoethyl ether of resorcin.

Properties of the Barium Salt.—It crystallizes from alcohol in fine yellow needles. It is nearly insoluble in water, whether hot or cold, but soluble in alcohol. It is stable at 100°, but if heated suddenly to a high temperature it explodes. Acetic acid does not decompose it.

The free bromdinitromonoethyl ether of resorcin was obtained by heating the barium salt with an acid; after recrystallization from alcohol it melted constant at 78°. It forms long, white, feathery needles, which turn yellow on standing.

The experiments just described make it highly probable that the substance melting at 58° and insoluble in water is the bromdinitroresorcindiethyl ether. There were also other products of the reaction, as the soluble salts obtained gave a test for nitrite as well as for bromide, but they were formed in such small quantity that it did not seem to us worth while to undertake the study of them.

CXXVI.—SYMMETRICAL TRIIODBENZOL.[1]

By C. Loring Jackson and G. E. Behr.

So far as we can find, three triiodbenzols have been described in the chemical literature, but the constitution of only one has been established thoroughly; this is the unsymmetrical (1.2.4) isomer, melting at 76° obtained by Kekulé[2] from the action of iodine and iodic acid on benzol. More recently Hantzsch[3] has also made it from the diioddiazobenzol iodide prepared from diiodaniline and found that it melts at 77°.

The other two isomeric triiodbenzols were made by Istrati and Georgescu[4] by heating together benzol, iodine and concentrated sulphuric acid. Unfortunately their original paper is not at our disposal, so that we know their work only from the abstracts of it in the "Jahresbericht über die Fortschritte der Chemie" and Beilstein's "Handbuch" (third edition). From these it appears that they ascribed the unsymmetrical constitution (1.2.4) to their compound melting at 85°, and the adjacent structure (1.2.3) to that melting at 182° to 184°, but there is no statement that they determined these constitutions experimentally. The experiments of Kekulé and Hantzsch just cited prove that the unsymmetrical isomer melts at 77° (or 76°) and, therefore, their compound melting at 85° cannot have this structure.

Under these circumstances it seemed worth while to prepare the symmetrical triiodbenzol and to determine its constitution by experiment; accordingly, we made the triiodaniline by the method of Michael and Norton,[5] that is, treating chloride of aniline with monochloride of iodine; and replaced the amido group in this body by hydrogen by means of the diazo reaction. The triiodbenzol thus obtained melted at 181°, which suggested that it was identical with the substance made by Istrati and Georgescu melting at 182° to 184°, and this was proved to be the case by treating it with fuming nitric acid, which converted it into a triioddinitrobenzol melting at 210°, whereas Istrati and Georgescu[1] under similar conditions obtained from their substance a dinitro derivative melting at 210° to 212°. That our triiodbenzol had the symmetrical constitution (1.3.5) was very probable, because the trichloraniline and the tribromaniline made under similar conditions are symmetrical compounds; but, as we felt it was necessary to give an absolute proof of its structure, we treated the triioddinitrobenzol with aniline, when it formed a trianilidodinitrobenzol melting at 181°. The symmetrical trianilidodinitrobenzol made by Palmer and one of us[2] from symmetrical tribromdinitrobenzol melted at 179°; in spite of the difference of 2° in these melting-points there can be no doubt of the identity of the compounds, and it follows, therefore, that the triiodbenzol melting at 181° has the constitution $I_3$1.3.5. This would leave only the structure 1.2.3 for Istrati and Georgescu's triiodbenzol melting at 85°; but in view of the fact that this compound was isolated from a mixture of the two triiodbenzols and two tetraiodbenzols, it seems to us possible that it may be the unsymmetrical isomer (1.2.4) (melting at 77°) contaminated with some of these less fusible substances. We had hoped to prepare several derivatives of the triiodbenzol, but were unable to do so in the time at our disposal, and, as we cannot continue our work together, we think it well to publish this account of the results so far obtained.

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[1] Presented to the American Academy of Arts and Sciences, December 12, 1900.

[2] Ann. Chem. (Liebig), **137**, 164 (1866).

[3] Ber. d. chem. Ges., **28**, 684 (1895).

[4] Buletinul Soc. d. Sciinte d. Bucuresci, I, 62; Jahresb. Chem., 1892, 1063; Beilstein's "Handbuch" (3d Edition), III, 73.

[5] Ber. d. chem. Ges., **11**, 111, (1878).

Preparation of Triiodaniline.

The triiodaniline was prepared by the method of Michael and Norton[3] slightly modified. Ten grams of aniline were dissolved in dilute hydrochloric acid, and diluted with water at 15° or a higher temperature to the volume of 7 liters. This solution was then treated with a rapid stream of air charged with the vapor of monochloride of iodine by passing it through a flask containing somewhat more than the required amount of this substance heated to about 60° by immersion in warm water. After thirty or forty minutes the action had come to an end, and the liquid was filtered as quickly as possible to remove a heavy black precipitate which had formed; the filtrate was allowed to stand for several hours, when it deposited a flocculent, buff-colored precipitate, the weight of which varied from 10 to 20 grams in different operations; that is, 20 to 40 per cent of the theoretical yield. An additional amount of the triiodaniline could undoubtedly have been obtained from the black precipitate, which was filtered out at first, but this was so impure that it seemed that more time would be lost in purifying it than in preparing fresh quantities of the second buff-colored precipitate, which, without further treatment, was pure enough for the manufacture of the triiodbenzol. That it was the triiodaniline was shown by an analysis of the substance purified by crystallization from glacial acetic acid and alcohol with the aid of bone-black, which gave 81.25 per cent of iodine instead of the 80.87 per cent required by the formula. Its melting-point was 185°. Michael and Norton give 185°.5.

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[1] Bul. Soc. Sci. d. Bucuresci, I, 66.

[2] This JOURNAL, II, 455.

[3] Ber. d. chem. Ges., II, III (1878).

The monochloride of iodine used in this work was made by the action of chlorine on iodine according to one of the methods given by Hannay,[1] and used later by Bornemann.[2] Bunsen's[3] method, which consists in boiling iodine with aqua regia, gave a less satisfactory result. Distillation of iodine with potassic chlorate, recommended by Schützenberger[4] and Hannay,[5] was not tried. Forty-two grams of powdered iodine (the amount needed for 10 grams of aniline) was treated with dry chlorine in a flask, until it had gained 12 grams; in addition to the reddish-brown liquid monochloride a considerable amount of the brilliant-yellow, crystalline trichloride of iodine was formed, which was converted into the monochloride by adding a small excess of iodine and heating the flask gently on the steam-bath under a short air condenser until the yellow crystals had disappeared. The monochloride of iodine solidified in fine gray crystals, if cooled below 10°, and in this solid state could be kept for some time without decomposition. Its tendency to solidify made it necessary, in the preparation of triiodaniline, to use the solution of chloride of aniline at a temperature of at least 15° in order to avoid the danger of having the tube stopped up with monochloride of iodine. Although this substance melts at 24°.7 (Hannay), we found no trouble from solidification with a solution at 15°, which can be explained by the marked tendency of the monochloride to remain liquid after it has been melted.

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[1] Proc. Lond. Chem. Soc., **26**, 815 (1873).

[2] Ann. Chem. (Liebig), **189**, 184 (1877).

[3] Gmelin-Kraut's "Handbuch," I, 2, p. 416.

[4] Ztschr. Chem., **6**, 1.

[5] Proc. Lond. Chem. Soc., **26**, 815 (1873).

Symmetrical Triiodbenzol,

$C_6H_3I_3$.

This substance was prepared as follows: Ten grams of the buff-colored triiodaniline, made as described in the previous section, were boiled with 125 cc. of benzol and 25 cc. of alcohol, and disregarding the undissolved portion, 5 cc. of commercial sulphuric acid were added, and then 5 grams of finely powdered sodic nitrite were sifted into the liquid as quickly as possible. As soon as the evolution of nitrogen had slackened sufficiently the liquid was boiled for some time on the steam-bath until a large part of the solvents had passed off; during this boiling a bright-yellow solid, which formed on the particles of sodic nitrite as they entered the liquid, changed its color to a light grayish-brown. After the solution had been boiled it was allowed to stand over night, and then the deposit was filtered out and washed, first with alcohol and afterwards with hot water, to remove the inorganic salts. The amount of this crude product rarely fell below 50 per cent of the theoretical yield.

The product, obtained as described above, was next sublimed from a large watch-glass heated on the sand-bath, and covered with a funnel which stood on a piece of filter-paper above the substance. If this sublimation was carried on slowly enough, as much as 80 per cent of white, glistening crystals was obtained, but if it was urged too fast the impurities also sublimed, and the crystals were yellow, or even in extreme cases light-brown and sticky. When proper care was used, white crystals were obtained by this sublimation, even from very impure products, such as those recovered by evaporating the liquid portion of the product of the diazo reaction. The white sublimed crystals were not, however, pure, and to remove from them a persistent impurity we found repeated recrystallizations from alcohol were necessary, which finally raised the melting-point to 181°, where it remained constant. The substance was then dried at 100° and analyzed with the following results :

I. 0.1187 gram substance gave, by the method of Carius, 0.1838 gram AgI.

II. 0.1453 gram substance gave 0.2249 gram AgI.

	Calculated for $C_6H_3I_3$.	Found. I.	II.
I	83.54	83.66	83.60

Properties of 1.3.5-Triiodbenzol.—This substance crystallizes from alcohol at first in radiating groups composed of a few slender prisms, which develop later into long, white prisms, frequently tapering, but always terminated by a single plane at an oblique angle to the sides of the prism. It melts at 181° and sublimes easily. It is freely soluble in benzol or carbonic disulphide even in the cold; in chloroform it is moderately soluble in the cold, freely soluble when hot ; in ether it is moderately soluble whether hot or cold ; in glacial acetic acid or ethyl acetate it is somewhat soluble in the cold, freely soluble when hot ; in alcohol or acetone it is slightly soluble in the cold, moderately soluble when hot ; it is apparently insoluble in water, hot or cold. The best solvent for it is alcohol. Strong hydrochloric acid has no apparent action on it, even when hot ; strong nitric acid also has little or no action on it, but fuming nitric acid acts on it in the way described in the next paragraph. Strong sulphuric acid, when heated with it to its melting-point, causes a partial decomposition, taking on a dark color ; at higher temperatures the triiodbenzol sublimes out of the mixture. A strong solution of sodic hydrate seems to have no action on it, even when boiling.

An attempt was made to prepare triiodnitrobenzol ; for this purpose 5 grams of symmetrical triiodbenzol were boiled with 140 cc. of a mixture consisting of 4 parts of fuming nitric acid with 1 part of common nitric acid. On cooling, light-yellow crystals appeared, and an additional amount of the product was obtained by pouring the acid liquid into about 1 liter of water, when a pale-yellow flocculent precipitate was formed, which was filtered out, after it had stood some time, and with the crystals weighed 5.3 grams. This was purified by crystallization from a mixture of 4 parts of alcohol with 1 of water, until it showed the constant melting-point 210°. This indicates that the substance is triioddinitrobenzol, since Istrati and Georgescu[1] obtained a triioddinitrobenzol melting at 210° to 212° from their triiodbenzol melting at 182° to 184°. For still greater certainty the substance was dried at 100° and analyzed with the following result:

0.2049 gram substance gave, by the method of Carius, 0.2644 gram AgI.

	Calculated for $C_6HI_3(NO_2)_2$.	Found.
I	69.77	69.76

The substance, therefore, is a dinitro compound, although obtained from fuming nitric acid somewhat diluted with common nitric acid. We did not have time to try whether the mononitro compound could be obtained with a still more dilute nitric acid.

The agreement between the melting-points of our triiodbenzol, 181°, and triioddinitrobenzol, 210°, with those obtained by Istrati and Georgescu,[2] 182° to 184° and 210° to 212°, establishes the identity of these substances beyond a doubt. The triioddinitrobenzol also gives us the means of proving their constitution. For this purpose 0.5 gram of the triioddinitrobenzol were heated with 0.5 gram of aniline; this proportion gives about 6 molecules of aniline to each molecule of the dinitro compound. The heating was carried on for two hours on the steam-bath, and the product, a dark-red solution, was freed from the excess of aniline by washing with dilute hydrochloric acid, when it formed a dark-red, sticky mass, which was purified by working it well with a rod under dilute hydrochloric acid and then crystallizing it from alcohol. It showed the constant melting-point 181°, which agrees sufficiently well with 179°, that given by Palmer and one of us[1] for the trianilidodinitrobenzol made from the tribromdinitrobenzol $Br_3 1.3.5.(NO_2)_2 2.4$. This proves, therefore that the triiodbenzol melting at 181° has the iodine in the position 1.3.5, as would have been inferred from its preparation from triiodaniline, which, according to the analogy of the chlorine and bromine compounds, should have the symmetrical constitution.

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[1] *Loc. cit.*, I, 66.

[2] *Ibid.*, I, 62, 66.

CXXVII.—A STUDY OF GROWING CRYSTALS BY INSTANTANEOUS PHOTOMICROGRAPHY.[2]

BY THEODORE WILLIAM RICHARDS AND EBENEZER HENRY ARCHIBALD.

Countless observers have watched the growth of crystals under the microscope. As long ago as 1839 attempts were made to study also the birth of crystals, in order to determine in what manner the new phase makes its entrance into the system. With a microscope magnifying 600 diameters, Link[3] thought he could detect the formation of minute globules at the moment of precipitation—globules which soon joined and assumed crystalline form. Schmidt,[4] Frankenheim,[5] and especially Vogelsang,[6] made similar observations some years later, and several more recent accounts of this phenomenon have appeared. Modern investigators have been more concerned with the speed of separation from supersaturated or supercooled liquids than with the form of the first separation.[7]

Ostwald, in 1891, accepted the interpretation of these data which assumes that crystallization is always preceded by the separation of an initially liquid phase, consisting of a supersaturated solution of the former solvent in its former solute.[1]

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[1] This JOURNAL, **11**, 455.

[2] Presented to the American Academy of Arts and Sciences, January 9, 1901.

[3] Pogg. Ann., **46**, 258 (1839).

[4] Ann. Chem. (Liebig), **53**, 171 (1845).

[5] Pogg. Ann., **111**, 1 (1860).

[6] Die Krystalliten (Bonn, 1875). See Lehmann, Molecularphysik, I, p. 730 (1888).

[7] Gernez: Compt. rend., **95**, 1278 (1882); Moore: Ztschr. phys. Chem., **12**, 545 (1893); Friedländer and Tammann: *Ibid.*, **24**, 152 (1897); Tammann: *Ibid.*, **25**, 441, **26**, 307, 367, **28**, 96; Küster: *Ibid.*, **25**, 480 **27**, 222; Bogajavlensky: *Ibid.*, **27**, 585.

This explanation is indeed a plausible one, and undoubtedly holds true in cases like those studied by Schmidt and Vogelsang, where a substance separates at a temperature not far below its melting-point, and often where a substance soluble in one liquid is precipitated by the addition of a consolute liquid in which the substance is insoluble. For example, phenol always separates from aqueous solution in the form of a liquid, and manganous sulphate forms at first two liquid phases when alcohol is added to its aqueous solution. On the other hand, the separation of a high-melting salt like baric chloride from its solution in pure water is much less likely to take place in this way. In the absence of data, the behavior of such a system is rather a matter for speculation than a question to be decided by reasoning.

Ostwald has shown that an exceedingly small particle of solid is capable of starting crystallization,[2] a fact which may not be wholly foreign to the present discussion.

In any case, the matter seemed worthy of further experimenting. Ostwald says: "Die erste Bildung der Krystalle lässt sich bei Salzlösungen und dergleichen microscopisch nicht verfolgen, weil gewöhnlich im Gesichtsfeld an einer bislang gleichförmigen Stelle plötzlich ein Kryställchen erscheint." While this is true as far as the human eye is concerned, instantaneous photography, an art unknown in Link's time, seemed peculiarly fitted for the unprejudiced recording of the circumstances attending the genesis of crystals. An attempt in this direction is described below.

The problem resolved itself into the taking of a number of successive instantaneous microphotographs of a suitable mixture at the point of crystallization. This problem presented some difficulties, however. In order to secure a sufficiently brief exposure very great illumination is needed. The greater the magnifying power of the lenses of the microscope-camera, the more intense must be the source of light. The difficulty is increased by the fact that most crystals are so transparent as to absorb but little light, and reflection is possible only in certain directions. Hence it is hard to obtain a distinct image even in a strong light. Moreover, the machinery necessary for shifting the plates must be so frictionless in construction, and so firmly fixed, as to impart no vibration to the camera or the mobile subject of study.

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[1] "Lehrbuch", I, 1039 (1891).

[2] Ostwald : Ztschr. phys. Chem., 22, 289 (1897).

These difficulties were at least partially overcome by two different arrangements, the first of which caused the successive impression of a bright image in a dark field, and the second registered dark images in a succession of bright fields. Obviously the former was the more economical as regards expenditure of sensitized film, and the simpler in execution; for when the field is dark successive images can be obtained by a very slight motion of either object or film, while, when the field is light, the whole previously exposed surface must be replaced by a fresh surface before each exposure.

The apparatus consisted of a good compound microscope fitted above with a vertical folding camera, which was supported by two massive steel pillars on the heavy stand. It was, in short, the regular photomicrographic outfit made by Bausch and Lomb. Between the microscope and camera, in a suitable light-tight box, was placed a revolving shutter, which allowed an exposure equal to one-fifth of the time of its revolution. Thus, when the shutter made two revolutions in a second, the exposure was one-tenth of a second. A Henrici hot-air motor, combined with speed-reducing double pulleys, enabled the experimenter to use any rate of revolution desired. The rate was reasonably constant, but no attempt was made to make it absolutely so. The sensitive plate or gelatin film was held above in a suitable holder, which was put in the place of the ground-glass plate used for focusing just before each series of exposures.

In carrying out the first of the two methods it was found more convenient to move the crystallizing solution than to move the photographic plate. For this purpose the slide bearing the drop of liquid was attached by a wire to a point just below the center of a segment provided above with saw teeth. The segment was moved gradually by the oscillating motion of a connecting rod, fastened by a crank to the revolving shutter at one end and playing into the saw teeth on the other. In order to make the motion certain, the stroke of the connecting rod slightly exceeded the distance between the saw teeth. The segment was suspended in such a way that its center of gravity coincided with its point of support, and the friction of its bearings was so adjusted that it would move easily, and yet remain stationary during the return stroke. The distance through which the observed object was moved was easily varied by altering the relative lengths of the lever-arms; distances varying from one-tenth to one-fiftieth mm. were generally used. The shutter was so arranged that during the exposure the segment and slide were at rest, the shift in position being effected during the four-fifths of the revolution through which the shutter was closed. The accompanying diagram will make the arrangement clearer.

The diagram represents the apparatus an instant before an exposure begins.

As a source of light any ordinary combination of incandescent electric lights proved to be inadequate. A good Auer von Welsbach light with a powerful reflector was more satisfactory, but the best results were obtained with the help of sunlight directed by a suitably arranged mirror and condensed by reflectors and lenses. The chief, though not serious, difficulty of this arrangement was the great heat caused by the converging rays, a difficulty which was obviated partially by an absorbent screen in some later experiments.[1]

The first photographs were taken by reflected light, the drop of solution being placed upon a ruby-colored slide. As soon as the crystallization had begun upon one edge of this drop the very sensitive plate was uncovered and the shutter and segment were set in motion. The exposure was stopped after 15 or 20 revolutions, so as to avoid confusing superpositions. Even with the strongest light the images were very faint and unsatisfactory; it is not worth the space to reproduce them here.

Another mode of obtaining light images on a dark ground, applicable to all except the isometric system of crystals, is the

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[1] Hutchins has shown that pure water is as good as a solution of alum for this purpose (Am. J. Sci., **143**, 526 (1892)).

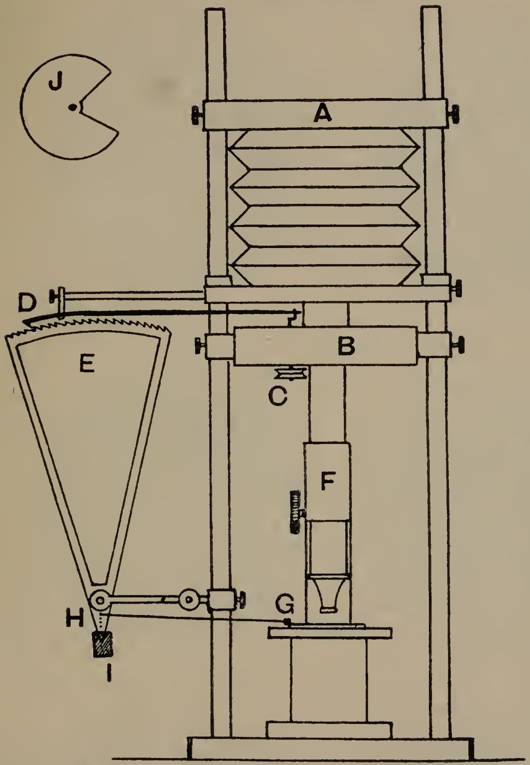

Fig. 1. Diagram of Photographic Apparatus. (One-sixth natural size.)

A, sensitive plate or film holder.

B, box containing shutter.

C, pulley attached to axle of shutter to communicate power from motor.

D, light rod moved by crank attached to same axle; D is guided by a stout support in which it moves loosely.

E, segment provided with rachet teeth; moved gradually by rod D.

F, microscope.

G, slide for object, moved by wire running to H.

H, holes to regulate amplitude of object's motion.

I, weight, balancing segment.

J, horizontal projection of revolving shutter in detail.

use of polarized light.[1] A Nicol prism was placed in the barrel of the microscope and another just below the stage. The main body of the light was thus intercepted by the crossed prisms, and only that which had been deflected by the crystalline structure was allowed to emerge. It is true that this method could not, in all probability, decide the chief point at issue; for the prenatal globular condition of crystals would probably have no effect on polarized light. Definite optical structure is of course necessary to produce the required deflection of the plane of polarization, and such definite structure might not be possessed by the globules. Nevertheless, the idea seemed well worth a trial.

The images were now much more clearly defined and striking, and with a magnification of 30 diameters, 10 sharp impressions, each exposed one-fiftieth second, could be obtained in a second. For this low power the eyepiece was removed from the microscope and an objective with long focal distance alone was used to give the image. The degree of enlargement was obtained by actually measuring the image of a micrometer scale divided into 0.1 mm. The rapidity of exposure was so great that many plates were sacrificed, for it was difficult to find the precise moment when nascent crystals were in the field of view. In most cases the crystallization was already well started when the exposure began, as in Fig. 4; but in some nothing but blank negatives were obtained. The best method is so to arrange circumstances as to have the crystallization begin upon one edge and spread slowly over the drop. Another difficulty was the attaining of the exact actinic focus, which differed slightly from the visual focus. It was found that a definite fraction of a revolution in the fine adjustment of the instrument or a definite shift of the sensitive plate could be relied upon to cover this difference, when experiment had once found the right spot.[2]

Among other substances sodic nitrate, baric chloride, cupric sulphate, and ferrous ammonic sulphate were found to give

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[1] This suggestion was kindly made by Prof. E. C. Pickering.

[2] Of course an apochromatic lens would have saved us this trouble, but our device answered sufficiently well and was less expensive. Such lack of definition as may be observed in the plates was due rather to the behavior of the object than to optical imperfection.

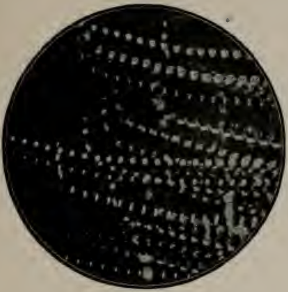

Fig. 2. Baric chloride; 30 diam.; exposure 0.04 sec.

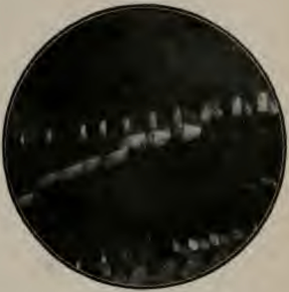

Fig. 3. Baric chloride; 30 diam.; exposure 0.08 sec.

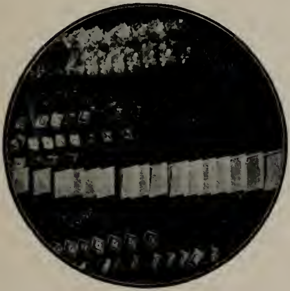

Fig. 4. Sodic nitrate; 30 diam.; exposure 0.10 sec.

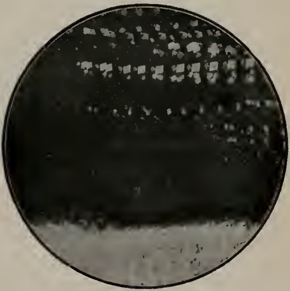

Fig. 5. Sodic nitrate; 30 diam.; exposure 0.12 sec.

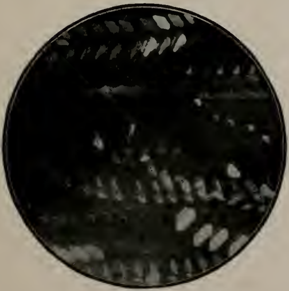

Fig. 6. Baric chloride; 110 diam.; exposure 0.10 sec.

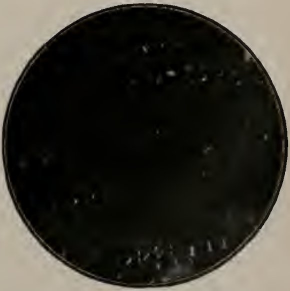

Fig. 7. Cupric sulphate; 110 diam.; exposure 0.12 sec.

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satisfactory results. A few photographs chosen as being typical examples of many negatives are given here. (Plate I. Figs. 2, 3, 4, 5.)

All the images recorded on these plates are perfectly sharp and regular when in focus; but the magnifying power was too low to give important evidence concerning the birth of the crystals. The crystals always first appear as points, indicating a diameter of less than $\frac{1}{300}$ mm. The regularity of growth of those already well started is worth a passing mention.

The next objective used gave a magnification of 110 diameters. With this power the light was so much diminished that exposures of less than one-fifteenth second became too pale. Three examples from among these negatives are given below. It will be noticed that in all cases the crystals have their regular forms when they first appear upon the plate. Another point worthy of attention is the fact that the growth in diameter at first is more rapid than it seems to be subsequently. This rapid growth of small particles has already been noticed by Ostwald;[1] it is treated more fully in the following pages. The crystals of sodic nitrate grew faster than those of baric chloride or cupric sulphate, and the two latter substances evidently appeared at first in very thin plates. It is interesting to note that the thickening of these plates caused a corresponding change in the quality of the emerging light, and hence the crystal images show a rhythm of dark and light. (Plate I., Figs. 6 and 7; Plate II., Fig. 9.)

At this point the whole method of procedure was changed on account of the probability that a globular condition, if it existed at all, would not be visible through the crossed Nicols. The apparatus was now arranged for the exposure of successive portions of a film to unpolarized sunlight emanating from a bright field, upon which the crystals appeared as dark spots. The slide and crystallizing solution were allowed to remain stationary, and the gelatin film was moved, as it is in the common film-cameras. The 2.5-inch Eastman cartridge film was found to answer the purpose. At first the turning was effected by an automatic electromagnetic arrangement which received its current from a make-and-break contact attached to the shutter. Since a current of 10 amperes was needed to secure a sufficiently forcible and speedy action, the operation of this device was somewhat troublesome, and when the exposures were not much more frequent than one a second the film was rolled by hand. A suitable signal attached to the shutter axle, which was still turned by the Henrici motor, gave the necessary indication of the proper moment for renewing the sensitive surface. With this apparatus it was of course possible to obtain photographs of isometric crystals, which could not be examined with the preceding arrangement.

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[1] Ztschr. phys. Chem., 22, 320.

At first a power of 100 diameters was employed, and very satisfactory pictures of the growth of crystals of potassic iodide were obtained. One of these negatives is reproduced here as an example. (Plate II., Fig. 9.) They showed nothing new, however; hence a much higher power of 580 diameters was applied by combining a "2-inch" eyepiece with an "$\frac{1}{8}$-inch" objective. With this contrivance the light was, of course, far less intense, and the definition less sharp. Even with the brightest sunlight, concentrated by mirrors and an Abbe condenser, the exposure could not profitably be made less than one-eighth second. These plates have been enlarged by usual processes to over seven times their original size, so that a total enlargement of over 4,000 diameters has been attained. Since these larger images were not much more clear than the smaller ones, while they occupy much more space, the plates herewith given are all from the original negatives.

A number of good impressions of crystallizing potassic iodide were taken under these circumstances, but many other rolls were sacrificed. The chief difficulty, as before, was to secure the right moment, and this difficulty was, of course, much augmented by the limited expanse of the field. Prints from a few of the successful negatives are given below. In order to give a clear impression in printer's ink, these were much intensified by successive photographic printing and intensification; but, of course, no attempt was made to remove the imperfections of the successive plates, for which allowance may easily be made. (Plate III., Figs. 10 to 15.)

Plate II.

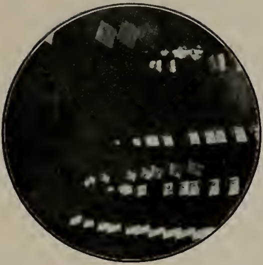

Fig 8. Sodic nitrate; 110 diam.; exposure 0.12 sec.

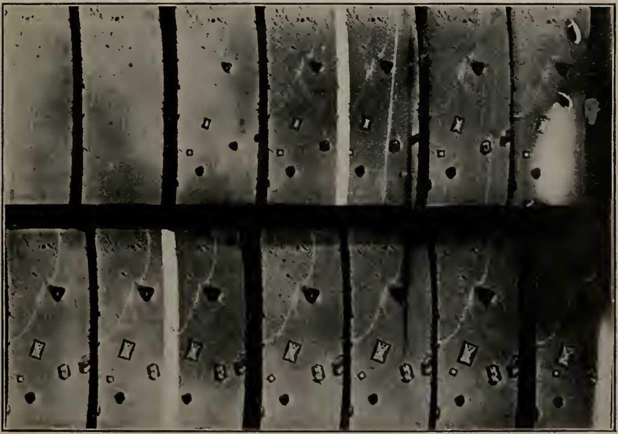

Fig. 9. Potassic iodide; 100 diam.; exposure 0.25 sec.

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The study of these photographs reveals several interesting points. In the first place, it is noticeable that no image is wholly without evidence of crystalline structure. The most doubtful cases are those in Figs. 9 and 11; but the elongated shape of these doubtful images seems to indicate a solid. A globule of a new liquid phase, $\frac{1}{1000}$ mm. in diameter, would have left an unmistakably circular image on the highly magnified plate, for its index of refraction could not have been identical with that of the aqueous solution. The fact that we could not find such a globule, of course, does not prove that a globule cannot exist, either for an infinitesimally brief period of time, or of an infinitesimal magnitude beyond the reach of microscopic observation. Nevertheless, so many scores of photographs were taken as to diminish considerably the probability that such globules can ever be seen with substances possessing a high melting-point.

A striking fact to be noticed in nearly all the most highly magnified records is the ill-defined appearance of the smallest crystals. This appears to be due, not to a lack of structure, but rather to the rapid growth in diameter, which is manifest in the young crystal. The initial rapidity is so great that the fifth of a second appears to include several different stages of growth, and hence a blurred impression results. It is easy to obtain some idea of the rapidity of this initial growth by comparing the sizes of the first two or three appearances of each crystal.

With this object a few of the series were measured by means of an accurate micrometer; but the conditions of the experiments are too uncertain to give the very precise measurements much value. Perfect constancy of temperature and evaporation, as well as in the rate of the revolving shutter, involving grave complications in the apparatus, should of course be maintained if great accuracy is attempted. Measurements with a fine millimeter scale afford all the precision which it is worth while to attain under present conditions. A typical case (Fig. 9, largest crystal) gave the following measurements in millimeters for the successive longest diameters: 2.0, 2.6, 3.0, 3.2, 3.3, 3.5, 3.7, 3.9, 4.1, 4.2, 4.4. The actual sizes of the crystals were, of course, only a hundredth of these measurements, since the enlargement was 100 diameters.

In spite of the inexact nature of such measurements, it is possible to use them as a means of defining approximately the law regulating the changes in speed. The following table details six series of corresponding diametric measurements of six crystals taken at random. The measurements were taken directly from the photographs in millimeters.

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.
First appearance	1.0	2.0	3.0	3.0	4.0	2.5
Second "	1.6	2.6	5.7	6.0	6.7	3.5
Third "	1.7	3.0	6.8	7.0	7.8	4.1

These all show greater growth in the first interval than in the second. In order to reduce them to one standard, the diameter of the third appearance was taken in each case as unity. The table then becomes :

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.	Average.
First appearance	0.59	0.67	0.44	0.43	0.51	0.61	0.54
Second "	0.94	0.87	0.84	0.86	0.86	0.85	0.87
Third "	1.00	1.00	1.00	1.00	1.00	1.00	1.00

At the time of the first appearance the average age of the crystal must be about half the time intervening between two exposures ; for the crystal must have been formed since the last exposure, and it is as likely to come near the beginning as near the end of the interval. Thus, in Fig. 11 the crystals evidently started immediately after the previous exposure, while in Fig. 9 they were registered while still very young. The averaging of a much larger number of observed diameters led to the slightly different values given below, corresponding to the accompanying times :

Time = t.	Diameter = D.
0 interval	Diameter 0
0.50 "	" 0.57
1.50 intervals	" 0.87
2.50 "	" 1.00

These data are plotted in Fig. 16.

Plate III.

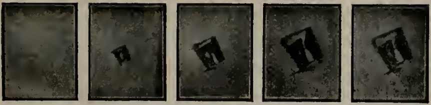

Fig. 10. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

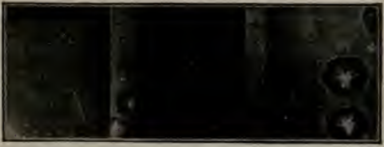

Fig. 11. Potassic iodide ; 580 diam. ; exposure 0.25 sec.

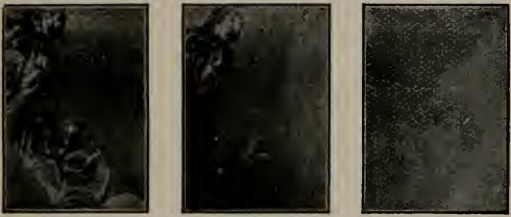

Fig. 12. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

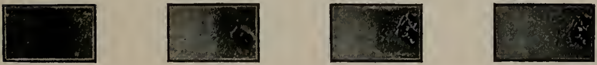

Fig. 13. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

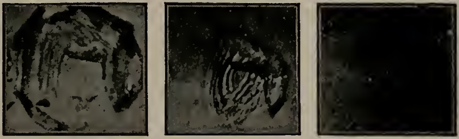

Fig 14. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

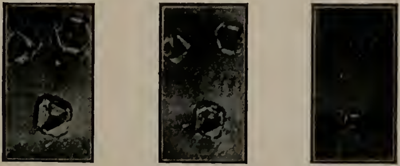

Fig. 15. Potassic iodide ; 580 diam. ; exposure 0.17 sec.

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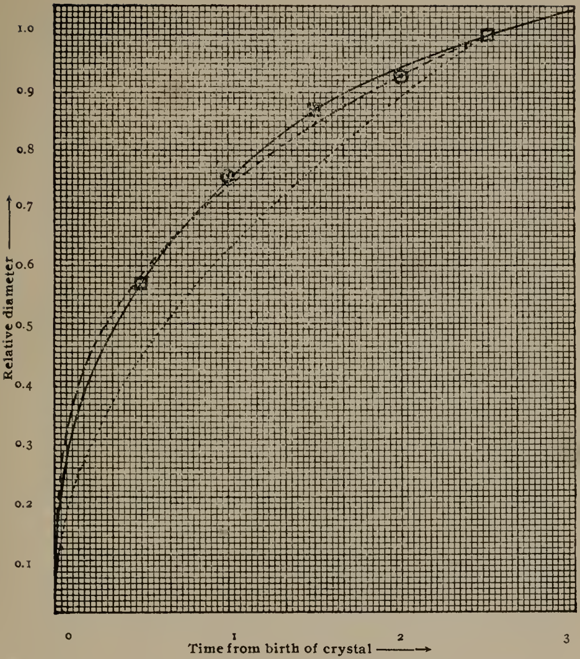

Fig. 16. Diagram Representing Rate of Increase in Crystal Diameter.

☐ represents point from average of crystals taken at random.

O represents point from average of selected crystals.

——— represents probable actual rate of growth.

- - - represents equation $D^3 = kt$.

...... represents equation $D^2 = kt$.

The unit of time is the time of one revolution of the shutter, or 1.25 seconds.

The substance was potassic iodide.

The inspection of the figure shows at once that the curve is similar in general shape to one represented by the equation $D^n = kt$, where D is the diameter of the crystal, t the time from the birth of the crystal, and k a constant. The only question is as to the magnitude of n. The curves which result from the assumptions $n = 2$ and $n = 3$ are given above, for comparison with the experimental curve. It is clear that the curve with the latter value, $n = 3$, is the nearest, possessing the same general curvature, and deviating from the average less than the individual measurements do. This is equivalent to saying that *equal increments of time correspond to equal increments of volume*, instead of equal increments of *surface*, as one might have supposed. Of course a law based upon such merely approximate data cannot be considered as definitely settled; but clearly the general character or tendency of the curve is established. It is probable that under the necessarily ill-defined conditions of our experiments the growth follows no one law with precision; supersaturation, convection, diffusion, and evaporation must all influence the result. The crystal which seems to have deviated most widely from the average is that depicted in Fig. 10; this crystal grew at first less rapidly than usual, and finally came almost to a standstill. It is possible that an increasing solubility due to increasing temperature may have caused this delaying tendency.

It is interesting to compare this average, calculated on the assumption that the crystal starts in the middle of the dark interval, with a few single cases which appear to have begun to crystallize very near the beginning or end of the interval. In these cases, the first image of the crystal will appear either almost as large as the second image, or very small compared with it. It will appear almost as large as the second image when the preceding exposure has just not caught the beginning of the crystal, which has thus had a whole interval for growth; or very much smaller than the second image when the first impression has registered a crystal only a very small fraction of a second old. Marked examples of the former case are to be found in Fig. 11, and of the latter in the largest crystal in Fig. 9, and the smallest crystal in Fig. 15. The times of revolution represented by Figs. 9 and 11 are the same, 1.25 seconds, and the other conditions also were identical, hence we may compare these with accuracy. Careful measurements of the sizes in Fig. 9 showed the first large impression of the crystals to be about 80 per cent of the diameter of the next impression, and approximately the same relationship appears in Fig. 11. In order to find if this relationship corresponds with the equation $D^3 = kt$, the larger diameter is assumed to be 0.93, the theoretical value corresponding to two intervals of time, if that corresponding to two and one-half intervals is taken as unity. Hence the smaller one becomes 0.75, corresponding to one interval of time, a value, marked in a circle on the diagram, which is surprisingly near the cubic curve. Hence the equation $D^3 = kt$ is confirmed. That the same curve holds approximately for the further growth of the crystal is manifest by a quantitative study of Fig. 9 (Plate II.).

In this connection it is interesting to note that the crystal seems often to grow at first in the same proportion in all directions. Even the very minute image in the center of the second exposure, given in Fig. 9, shows itself under the microscope to be elongated like the crystal which grows from it. In the next exposure this crystal had the proportions 0.02 mm. × 0.0125 mm., and after four more exposures it still had almost exactly the same proportions, being 0.035 mm. × 0.022 mm. After two or three more seconds the form given in Fig. 9 began to change slightly, the crystal becoming slightly less elongated in shape; but by this time the neighboring crystals had grown so much as to approach it, and hence to alter the conditions. A similar constancy in proportion may be observed in many other series here given.

The diagram shows how exceedingly fast the diametric growth of the crystal must be in the first tenth of a second of its existence. Hence we have an explanation for the suddenness of its appearance to the eye of an observer, and for the blurred edges of its photographic image. It is true that another cause may contribute to the blurred effect; namely, the irregular refraction caused by the convection of the lighter solution which has just deposited part of its load; but the speedy growth alone is capable of explaining the observed indistinctness.

Interesting as the rapid initial growth in diameter may be, it places a serious bar in the way of more precise study of the birth of crystals. One clearly needs not only high magnifying power but also great speed; and these two together require very intense light. Whether or not we shall be able to obtain more positive knowledge with the present apparatus is questionable. The same phenomenon casts a measure of doubt over some of the observations of Link and his followers. Is it not possible that the subjective effect of the rapidly growing crystal might be mistaken for that of a globule of liquid? Even upon the photographic plate there is a slight resemblance, and in one or two cases deliberate study is needed to detect evidence of structure in the smallest crystals.

In conclusion, the report of the foregoing pages may be summarized as follows: It has been found possible to take very frequent photomicrographs of crystals during their birth and growth. An enlargement of over 4,000 diameters was obtained, and both common and polarized light were used. Only substances with high melting-points were examined, and the crystallization was always from aqueous solution. No properly focused image on any of the plates seemed to be devoid of crystalline structure. The growth in diameter during the first second of the crystal's life was found to be vastly greater than during the subsequent period. Not the diameter itself, but a power of the diameter, was proportional to the time under the conditions used in our experiments. This exceedingly rapid initial diametric growth accounts for a lack of definition noticed in the first images,—a lack of definition sufficient to have misled the eye, but not enough wholly to obscure the photographic evidence of crystalline structure.

Hence we may conclude that whatever theoretical reason there may be for believing that crystals always develop from a transitory liquid phase, the present experimental evidence is inadequate to prove that these globules attain a size visible in the microscope, except in the case of substances which melt at temperatures not far from the temperature of crystallization. The present paper is to be regarded rather as the suggestion of a mode of study than as a finished treatment of the subject, however.

The apparatus might be used to obtain a series of kinetoscopic pictures of insects or other small animals or plants, and is now being used for the study of the change in structure of steel at high temperatures. We are indebted to the Rumford Fund of the American Academy of Arts and Sciences for much of the apparatus used in this work.

CAMBRIDGE, MASS., October, 1898,
to October, 1900.

CXXVIII.—THE SOLUBILITY OF MANGANOUS SULPHATE.[1]

By Theodore William Richards and Frank Roy Fraprie.

The solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell,[2] and the present paper is written to confirm in some measure the results of his work. He was able to disprove, by well-considered experiment, the less recent work of Linebarger,[3] who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly acknowledged when it is supported, hence the publication of the present paper.

The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time.[4]

It was soon found that a much higher temperature was necessary to drive off the water of crystallization of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least 1 molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapor. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half an hour at 350° in an air-bath. In this respect the substance reminds one of cupric sulphate.[5] The amount thus retained does not much exceed the tenth of a per cent, and the effect upon Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a carefully watched naked flame, and applied after drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0.2 mg. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

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[1] Presented to the American Academy of Arts and Sciences, March 13, 1901.

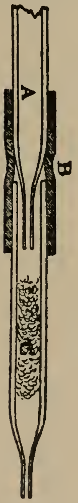
[2] J. Phys. Chem., 4, 637 (1900).

[3] This Journal, 15, 225 (1893).

[4] A brief statement of the scope and object of this work will be found in Proc. Am. Assoc. Adv. Sci., 213 (1898).

[5] Richards: Proc. Am. Acad., 26, 240 (1891).

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large, stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder.[1] The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analyzed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van 't Hoff's laboratory.[2] A diagram of the pipette is appended. The cotton was necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.



Filtering pipette.
The filtering attachment, filled with cotton wool ("absorbent cotton" C), is temporarily attached to the jet A of a 5-cc. pipette by means of the rubber tube B.

After filling the pipette and quickly removing the rubber filtering-jet attached to it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated, and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained :

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[1] Schröder: Ztschr. phys. Chem., **11**, 454 (1893); Noyes: *Ibid.*, **9**, 606 (1892). For details see Richards and Faber: This JOURNAL, **21**, 168 (1899).

[2] Van 't Hoff and Meyerhoffer: Ztschr. phys. Chem., **27**, 79 (1898).

The Solubility of $MnSO_4.5H_2O$ *at 25°.*

No. of determination.	Time of saturation. Hours.	Weight of solution. Grams.	Weight of $MnSO_4$. Grams.	$MnSO_4$ for 100 grams water. Grams.
1	6	5.0342	1.9849	65.09
2	6	6.3405	2.4947	64.89
3	8	4.4318	1.7470	65.07
4	8	5.2465	2.0656	64.94
Average,				64.99
5	48	3.4514	1.3622	65.20
6	72	3.5349	1.3947	65.17
Average,				65.19

Cottrell found 64.78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only two and one-fifth hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded below :

The Solubility of $MnSO_4.4H_2O$ *at 30°.15 and 35°.0.*

No. of determination.	Temperature.	Time of saturation. Hours.	Weight of solution. Grams.	Weight of $MnSO_4$. Grams.	$MnSO_4$ for 100 grams water.
7	30°.15	4	4.3125	1.7215	66.44
8	30°.15	4	5.7567	2.2943	66.27
9	30°.15	4	4.5992	1.8339	66.32
10	30°.15	4	5.2322	2.0894	66.48
Average,					66.38
11	35°.0	13	3.7009	1.5007	68.21
12	35°.0	14.5	2.7854	1.1296	68.22
Average,					68.22

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4.3 molecules of water for each $MnSO_4$, but it was, nevertheless, probably the designated hydrate containing included mother-liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from Determinations 11 and 12 contained 4.03 molecules of water.

The results at 30°.15, giving an average of 66.38, correspond almost exactly with Cottrell's figure, 66.43 at 30°; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67.87, and ours, 68.22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case; and the higher figures, other things being equal, would have been accepted as the more accurate.

While this may be true, the recent work of Ostwald[1] on the solubility of powders and the surface-tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapor-tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation.[1] In view of Ostwald's newer work it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it will simply hasten the speed of attaining saturation ; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $MnSO_4.H_2O$ attained a concentration of 57.41 grams in 100 grams of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72.5 to 62.3 grams per 100. The solubility found after twenty-seven hours, when both methods gave the same result, was 58.32, or 0.91 gram more than the first and 4 grams less than the second figure.

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[1] Ztschr. phys. Chem., 34, 495 (1900).

[2] For example, see "Ostwald's Physicochem. Measurements," Walker (Macmillan, 1894), p. 176.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained ; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Every one will agree with Ostwald in deciding that the solution-tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermostat, would perhaps be the safest apparatus, although complete saturation would require much time.[1]

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty; but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25° with both or either hydrate to yield 40.1 grams of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

CAMBRIDGE, MASS., February, 1901.

THE PREPARATION OF OSMOTIC MEMBRANES BY ELECTROLYSIS.

BY H. N. MORSE AND D. W. HORN.

The difficulties with which Pfeffer had to contend in the preparation of suitable semipermeable membranes for the investigation of osmotic pressure are well known and need not, therefore, be rehearsed. Yet, notwithstanding the importance of the subject, no suggestion appears to have been made up to the present time which has helped to obviate any of those difficulties or in any degree to lessen them. The method of Pfeffer has not been improved, and, judging from the testimony of many who have tried it, attempts to prepare the Pfeffer cell usually fail to give satisfactory results.

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[1] Richards: This JOURNAL, 20, 189 (1898).

In this connection, it occurred to the authors that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall. The results of our experiments in this direction appear to have justified the expectation and to be worthy of a brief preliminary notice.

The first problem concerned, of course, the effective removal of the air in the walls of the porous cups, since the presence of air obviously interferes with the formation of a sound membrane. For this purpose we have taken advantage of the strong "endosmose" which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the electrodes are immersed. A boiled solution of potassium sulphate containing about 0.5 gram of the salt in the liter was filled into the porous cup and into the beaker in which it was placed until the level of the liquid within and without reached nearly to the edge of the cup. On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner. As the liquid within the cup rose, it was removed from time to time with a pipette or by means of an intermittent siphon and replaced by pouring more of the solution into the liquid outside the cup. The quantity of water forced through the wall in this way was considerable. As a rule, we have continued the electrolysis of the sulphate until 300 cc. had been removed by the pipette or siphon, which required ordinarily about one hour. The cup was then emptied, washed, and placed in a large volume of distilled water until required for the deposition of the membrane.

To form the membrane, the wet cup was placed in a beaker and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with the dynamo so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution (N/10 or N/5 sulphate) and that of the potassium ferrocyanide (also N/10 or N/5) were introduced as nearly simultaneously as possible. At first there is considerable endosmose in the direction of the current, *i. e.*, from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. Both walls remained perfectly clean and free from discolorations except in a few instances, in which, for some reason not yet determined, metallic copper was deposited on the outside of the cup. At the upper edge of the cup, however, nearly midway between the two sides, there soon appears a line of reddish-brown color, showing in general the position of the membrane with respect to the outer and inner walls of the cup. The resistance usually rises quite rapidly, reaching in extreme cases 3,000 ohms within an hour, while the endosmose diminishes correspondingly. The most rapid rise in resistance is observed in the less porous hard-burned cups. In the softer and more porous ones, the resistance may not exceed 200 or 300 ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing apparently to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again.

Having obtained the desired resistance, the cell was removed, rinsed inside and out, filled with distilled water, and placed in a beaker containing water, care being taken, of course, not to allow any of the liquid from the inside to come in contact with the outer surface of the cup, and *vice versa*.

Our first experiments were with ordinary porous battery cups holding approximately 250 cc. On treating some of these in the manner described above until a resistance of from 1,500 to 3,000 ohms had been reached, they were tested as to the presence of a sound membrane within their walls by filling them one-third full of a normal solution of sugar and then immersing them in water until the liquids within and without were on the same level. The water entered quite rapidly and the cups usually began to overflow within from fifty to seventy-five hours. On breaking the cups, the membrane could be seen as a thin line along the fracture surfaces. Ordinarily it was located about midway between the two walls except where the material of the cup manifestly lacked uniformity. In such places the line would bend to one side or the other, and again return to its original direction beyond the uneven spots. The experiment was repeated with the same result with samples of all the various kinds of porous battery cups which had accumulated in the laboratory. It was found that a membrane which would at least exhibit osmotic activity could be made in the walls of any of them without difficulty. It was also tried with certain other cups which had been specially made with a view to the rapid filtration of liquids and which were, therefore, much more porous than the ordinary battery cup. We could form a membrane in these, but it was necessary to exercise some care in the control of the current. Otherwise the resistance would occasionally drop in a marked degree, indicating a rupture of the membrane. The resistance, in the case of the cups last mentioned, could not be raised above a certain point, which was far below that which could easily be obtained in less porous cups.

With a view to testing the power of the electrolytically prepared membrane to resist pressure, we had made at a local pottery some bottle-shaped cells having a capacity of about 250 cc. After depositing the membrane in these, in the manner described, they were filled with a normal solution of sugar, closed with rubber stoppers through which glass tubes had been passed, and placed in beakers of water standing upon the floor. Other lengths of tubing were added until the ceiling, 5.5 meters above the floor, was reached. Our tubes began to overflow in periods ranging from six to fifteen hours. When the open manometers were replaced by closed ones containing mercury, the cells failed; not, however, in consequence of ruptured membranes. In manufacturing such vessels, the bottom is made separately and is inserted and cemented in its place after withdrawing the mold upon which the rest of the bottle is formed. The union between the two parts proved to be a weak one in the case of our cells. Before any considerable pressures were reached the bottoms gave way, permitting the sugar solutions to escape. In most instances the line of detachment could be seen, but not in all. We therefore added a little ferrocyanide to the solutions of sugar and a little copper sulphate to the water in which the bottles stood in order to ascertain whether any of the sugar escaped at other places. A reddish-brown circular line then appeared where the two parts had been joined, but nowhere else.

Our next experiments were with small porous cups, such as are employed in making standard battery cells. These were about 85 by 25 mm., internal measurement, and were provided with a flange at the top. We had found by previous experience that the forcing of a stopper into a cell is liable to injure the membrane, hence we cemented glass tubes in the cups before forming the membranes. In order to make the union more secure, channels were cut on the inside of the cups a little below the rim and parallel to it. The glass tubes, 125 mm. long and with external diameters somewhat less than the internal diameters of the cups, were provided with rubber rings at one end, of such thickness that rubber and glass together made moderately tight stoppers for the cups. These were pushed into the cups until the upper edges of the rubber rings were a little below the channels. The spaces above the rubber were then filled with the cement, which was made by mixing 5 parts of litharge with 1 part of glycerine. After hardening for forty-eight hours, the exposed surface of the cement was painted, to protect it from liquids, with a solution of equal parts of rubber and paraffin in carbon bisulphide. The cups were then freed from air and the membranes deposited in the usual manner. When the rubber stoppers carrying the closed manometers were inserted, provision was made for the escape of the superfluous sugar solution by manipulating a small steel rod between the rubber and the glass. The rod was afterwards extracted with a pair of forceps. In the first cell prepared in this way the pressure rose within an hour to 3.25 atmospheres, when the stopper began to give way. It was again crowded into place, and the pressure rose to a little over 3.5 atmospheres, but from this point the stopper was slowly pushed out of the tube. We then emptied the cell and shrunk the end of the glass tube in the flame to about three-fourths its original diameter, in order to give the stopper a more secure hold in the glass. With this modification we were able to secure pressures a little above 4.5 atmospheres. At that pressure, however, the sugar solution always began to ooze out between the manometer and the rubber stopper, and the stopper itself to move upward out of the tube.

We have found it impossible, with the crude manometer hitherto employed by us, to test our membranes at pressures much above 4.5 atmospheres; and it is clear that, to do this, rubber stoppers must be dispensed with and some suitable metallic connection devised to join the manometer to the cell.

We have made no attempt as yet to measure osmotic pressure, our object at present being only to test the strength of the membranes. It seems improbable that the total osmotic pressure of concentrated solutions, *e. g.*, molecular-normal ones, will ever be directly measured. It should, however, be practicable to construct cells in which the pressure of dilute solutions can be quite accurately determined. In that case, it should be feasible to measure the pressures of more concentrated ones by a differential method. For example, having obtained a membrane of such quality in a cell of such construction that the osmotic pressure of a tenth-normal solution can be satisfactorily measured, the pressure of a two-tenths normal solution could be determined by immersing the cell, not in water, but in a one-tenth normal solution, etc. It is probably safe to predict that if a method of determining molecular weights or electrolytic dissociation, by measuring osmotic pressure, is ever worked out, it will be developed along this line. That is, differences of pressure rather than the enormous totals will be measured. It is hoped that the electrolytic method of making semipermeable membranes, when developed by further study, may do away with what has hitherto appeared to be an insurmountable obstacle in the way of progress in this direction.

Contributions from the Chemical Laboratory of Cornell University.

ON BILIRUBIN, THE RED COLORING-MATTER OF THE BILE.

BY W. R. ORNDORFF AND J. E. TEEPLE.

[PRELIMINARY PAPER.]

The bilirubin used in this work was prepared from ox gall-stones, which were sent to us by Mr. F. M. Bell, of the firm of Armour & Co., of Chicago. We desire here to express to this company our appreciation of their kindness and generosity to us. The work here given would have been impossible but for their aid in furnishing the gall-stones free of all charge. We have used 0.75 pound of the gall-stones in this investigation. The dried gall-stones were ground, sieved through a 30-mesh sieve, and after being placed in filter-paper cylinders, extracted with ether in a Soxhlet apparatus until exhausted (twelve to twenty hours). The material was then dried and exhausted with chloroform in the same way (thirty to forty hours); again dried, placed in a porcelain dish, and extracted with boiling distilled water until exhausted. The red-colored mass was then digested for several hours with an excess of dilute hydrochloric acid, washed by decantation until the filtrate was free from calcium and hydrochloric acid, dried thoroughly, and extracted in a Soxhlet apparatus, first with ether (two hours) then with absolute alcohol until the alcoholic filtrate had only a yellow color (six hours). After drying, the material was placed in a Soxhlet apparatus and exhausted with pure chloroform (one hundred and twenty-five hours). Fresh chloroform was used after every eight hours. The chloroform extracts, containing the bilirubin, were concentrated by distillation, the concentrated solution precipitated with absolute alcohol, and the mixture heated on the water-bath until all the chloroform had distilled off. The alcohol was decanted off and the precipitated bilirubin was boiled with absolute alcohol until exhausted. This bilirubin was found not to be completely soluble in chloroform. It was then dissolved in chloroform by heating to boiling with a large quantity of chloroform in successive portions, the solution filtered twice, concentrated, again precipitated by absolute alcohol, washed with alcohol, filtered, dried, and, if not completely soluble in chloroform, the process was repeated. All this work with chloroform and bilirubin was done in a photographic dark-room. Some of the product completely soluble in chloroform was then crystallized from pure dimethyl aniline (boiling-point 192°.2 to 192°.8 C.). This product, under the microscope, was beautifully crystallized in reddish-yellow needles and was homogeneous.

In order to determine whether the products were pure, the following analyses were made for us by Mr. G. W. Cavanaugh, of the Agricultural Experiment Station, to whom we wish here to express our thanks:

I. 0.269 gram bilirubin gave 17.7 cc. N/10 NH_3 or 0.02478 gram N.

II. 0.3444 gram bilirubin gave 22.7 cc. N/10 NH_3 or 0.03178 gram N.

	Calculated for $(C_{16}H_{18}N_2O_3)x$	Found.	
		I.	II.
N	9.81	9.21	9.23

No. II. was heated with the sulphuric acid for three-quarters of an hour longer than No. I. These analyses were made by the modified Kjeldahl-Gunning method, adopted by the Association of Official Agricultural Chemists, 1898, and given in Bulletin 46 (revised), page 17, of the U. S. Department of Agriculture, Division of Chemistry. The formula generally accepted for bilirubin $(C_{16}H_{18}N_2O_3)_x$ requires 9.81 per cent N.[1] Suspecting some loss of nitrogen by this method, we then made an analysis by the Chenel[2] modification of the Kjeldahl method and obtained the following result:

0.2158 gram bilirubin gave 14.12 cc. N/10 NH_3 = 0.01982 gram N or 9.19 per cent N.

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[1] The atomic weights used in this paper are those recommended by the committee of the German Chemical Society. Ber. d. chem. Ges., **31**, 2761 (1898).

[2] Bull. soc. chim. (Paris), 1892, [1], 321.

All three of these analyses were made with the bilirubin crystallized from dimethyl aniline. This product was completely soluble in chloroform and left no ash on ignition.

We next determined the nitrogen by the absolute method, using marble (which had been boiled for a long time with water to remove air) and dilute hydrochloric acid to generate the carbon dioxide. The following are the results with the same product analyzed by the Kjeldahl method :

I. 0.2208 gram bilirubin gave 19.2 cc. N at 732 mm. bar. (corrected) and 24°.5 C.

II. 0.1728 gram bilirubin gave 15.25 cc. N at 729.8 mm. bar. (corrected) and 26° C.

I.	II.
9.36	9.39

As we found it absolutely impossible to get carbon dioxide free from air from marble we made it by the action of boiled dilute sulphuric acid on a boiled solution of sodium bicarbonate. Using the product crystallized from dimethyl aniline and completely soluble in chloroform we obtained the following result :

0.1659 gram bilirubin gave 14.2 cc. N at 733.95 mm. bar. (corrected) and 25°.8 C. or 9.17 per cent N.

We next used magnesite to develop the carbon dioxide. This was heated in a hard-glass tube on a separate small combustion furnace. Following a suggestion of Professor Morse, we heated the copper oxide and the reduced copper spiral in the combustion tube in an atmosphere of carbon dioxide and allowed it to cool in the same gas in order to expel occluded air. A specimen of crystallized bilirubin, which was not completely soluble in chloroform, but left an infinitesimal residue, gave the following result :

0.1659 gram bilirubin gave 14.2 cc. N at 748.8 mm. bar. (corrected) and 27° C. or 9.3 per cent N.

Another analysis of a product precipitated from chloroform by alcohol, and completely soluble in chloroform, resulted as follows :

0.2084 gram bilirubin gave 17.45 cc. N at 742 mm. bar. (corrected) and 24° C. or 9.16 per cent N.

None of the products analyzed left any ash on ignition, and all were dried to constant weight at 130° C. before being analyzed.

Averaging the three results by the Kjeldahl method, gives 9.21 per cent N, while the average of the five results by the absolute method is 9.28 per cent N. If we omit the two results by the absolute method (9.36 and 9.39), where we used marble to develop the carbon dioxide (which we proved to contain air), the average of the three remaining results is 9.21 per cent N. These results agree very well with that recently obtained by v. Zumbusch[1] on bilirubin crystallized from dimethyl aniline and analyzed by the Kjeldahl method. He obtained 9.3 per cent N. Recalculating this from v. Zumbusch's data, using the same atomic weights we have specified above, would give 9.26 per cent N.

Having thus shown that our product was pure and that the formula for bilirubin, $(C_{16}H_{18}N_2O_3)_x$, is not correct, we next determined the amount of carbon and hydrogen in bilirubin, using the method given in Gattermann's Praxis des organischen Chemikers (third edition), for analyzing organic compounds containing nitrogen. Using the product precipitated from chloroform by alcohol, perfectly soluble in chloroform, and dried at 130°, we obtained the following result:

0.205 gram bilirubin gave 0.5048 gram CO_2 and 0.1133 gram H_2O = 67.15 per cent C and 6.19 per cent H.

With the product crystallized from dimethyl aniline, which was not completely soluble in chloroform, but left a minute residue (the same product which gave 9.3 per cent N (see above)), we found:

0.2336 gram bilirubin gave 0.5761 gram CO_2 and 0.1248 gram H_2O or 67.25 per cent C and 5.99 per cent H.

As it seemed possible from the results of Benedict[2] that the reduced copper spiral might have retained enough carbon dioxide or other carbon compound to vitiate the results, and, as it was also probable that any oxides of nitrogen which were not decomposed by the reduced copper spiral would also give high results for carbon, we next made two analyses by the Benedict[1] method of determining carbon and hydrogen in nitrogenous organic compounds. The following are the results on the product precipitated from chloroform by alcohol, completely soluble in chloroform and dried to constant weight at 140° C.:

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[1] Ztschr. physiol. Chem., **31**, 454.

[2] This Journal, **23**, 343.

	Weight bilirubin.	Weight sugar.	CO_2 found.	CO_2 from sugar calculated.	CO_2 from bilirubin.	H_2O found.	H_2O from sugar calculated.	H_2O from bilirubin.
I.	0.2594	0.1270	0.830	0.19595	0.63405	0.2078	0.07355	0.13425
II.	0.3025	0.1348	0.9504	0.2080	0.7424	0.23995	0.07805	0.1619

In percentages these results are for No. I: C = 66.66, H = 5.80; for No. II: C = 66.93, H = 6.00.

At our request Dr. F. G. Benedict, of Wesleyan University, Middletown, Conn., made two analyses of this same bilirubin for us by his own method. We desire here to thank Dr. Benedict for his kindness in this matter. The following are the results he obtained:

	Weight bilirubin.	Weight sugar.	CO_2 found.	CO_2 from sugar calculated.	CO_2 from bilirubin.	H_2O found.	H_2O from sugar calculated.	H_2O from bilirubin.
I.	0.1504	0.1126	0.5411	0.1737	0.3674	0.1543	0.0652	0.0891
II.	0.1512	0.1017	0.5253	0.1569	0.3684	0.1409	0.0589	0.0820

Or, in percentages, C = 66.62, H = 6.64 for No. I; and C = 66.45, H = 6.08 for No. II. A check analysis of the sugar resulted as follows:

0.2026 gram sugar gave 0.3123 gram CO_2 and 0.1181 gram H_2O.

	Calculated for $C_{12}H_{22}O_{11}$.	Found.
C	42.07	42.04
H	6.49	6.50

Averaging these four results gives 66.66 per cent C. and 6.13 per cent H. If we omit the result H = 6.64 per cent (which is manifestly too high), we obtain 5.96 per cent H as the average of the three determinations. Since 1864, when Städeler first obtained bilirubin pure, twelve analyses have been published. The average of these is C = 66.87 per cent and H = 6.36 per cent. The following table gives the percentages required by the various formulas and the averages found by us:

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[1] This Journal, 23, 343.

	I.	II.	III.	IV.	Found.
	$C_{16}H_{18}N_2O_3$.	$C_{25}H_{27}N_3O_5$.	$C_{34}H_{36}N_4O_7$.	$C_{34}H_{37}N_4O_7$.	Average.
C	67.07	66.755	66.61	66.50	66.66
H	6.35	6.07	5.94	6.09	5.96
N	9.81	9.37	9.17	9.155	9.21
O	16.77	17.80	18.28	18.255	18.17

Formula III agrees better with the average of the results found than any of the others. We have endeavored to determine the molecular weight of bilirubin, but so far without success.

We next heated the pure crystallized bilirubin, completely soluble in chloroform and dried at 130° C. with *pure* concentrated hydriodic acid according to the Zeisel method[1] for determining alkoxy groups. No silver iodide was formed, and hence bilirubin does not contain an alkoxy group, nor does it contain crystal alcohol.

When heated with hydriodic acid and ammonium iodide according to the method of Herzig and Meyer[2] for determining alkyl groups joined to nitrogen we obtained the following results:

I. 0.3125 gram bilirubin gave 0.120 gram AgI. Formula III. requires 0.1198 gram for one alkyl group.

II. 0.2845 gram bilirubin gave 0.1018 gram AgI. Formula III. requires 0.1091 gram for one alkyl group.

III. 0.2912 gram bilirubin gave 0.0966 gram AgI. Formula III. requires 0.1116 gram for one alkyl group.

I. and II. were made with the bilirubin crystallized from dimethyl aniline. It was completely soluble in chloroform and dried to constant weight at 120° C. III. was made with bilirubin precipitated from chloroform with alcohol. It was completely soluble in chloroform and dried to constant weight at 130° C. These results agree better with formulas III. and IV. than with any of the others.

When heated with zinc dust in an atmosphere of hydrogen, bilirubin gives products having the odor of an old pipe. Among these products the haemopyrrol of Nencki seems to be present. That bilirubin is a derivative of pyrrol there seems to be no doubt from the ease with which it unites with diazo compounds even in strong acid solution.

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[1] Monatsh. Chem., 6, 989.

[2] *Ibid.*, 15, 613.

Further work on bilirubin, especially with a view to determining its formula and constitution as well as its relations to hemoglobin, hematin, and hematoporphyrin will be undertaken in this laboratory.

CORNELL UNIVERSITY,
ITHACA, N. Y., June, 1901.

REVIEWS.

AN INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY, IN THE FORM OF POPULAR LECTURES SUITED FOR UNIVERSITY EXTENSION STUDENTS AND GENERAL READERS. By DR. LASSAR-COHN. Translated from the second German edition by M. M. PATTISON MUIR, M.A. New York : D. Van Nostrand Co. 1901. 348 pp. Price, $2.00.

As the first German edition of this book was reviewed in this JOURNAL, Vol. 23, page 88, the excellent English translation may be treated briefly.

In this unpretentious little volume, by omitting everything of lesser prominence and skilfully avoiding reefs and quicksands in chemical theory, the author has succeeded in giving a remarkably clear elementary sketch of inorganic, and of a little of organic, chemistry. The reader of to-day should be warned, however, that some may consider the title misleading, some, indeed, may consider the terms "old-fashioned" or "obsolete" more fitting than "modern," inasmuch as nowhere in the book is mention made of *the Ion*.

To those who can find profit in non-ionic chemistry, Prof. Lassar-Cohn's book is cordially recommended as one of the best, perhaps the best of its kind. E. R.

LE FLUOR ET SES COMPOSÉS. Par HENRI MOISSAN. Paris : Steinheil. 1900.

The student who consults this book, expecting to find a dry monograph, will continue to read it with the feeling that he is enjoying a delightful account of a voyage of discovery. The author has been over all the ground himself, often as the pioneer, and he tells about it in that clear, concise, and easy manner which distinguishes him even among French scientists.

The book is divided into seven chapters and a bibliography. The first chapter treats of the isolation of fluorine. The experiments of Davy, Aimé, the Knox Brothers, Louyet, Fremy, and Gore are discussed and the reasons for their failure pointed out. The author's unsuccessful experiments are frankly stated, and we learn that the isolation of fluorine was not a lucky accident but the result of years of work. Some of the compounds with which he worked were extremely poisonous and he was compelled to stop no less than four times on account of fluoride of arsenic alone. The apparatus originally used is described in the first chapter, though the second is devoted to new forms of apparatus for obtaining fluorine. The platinum in the original model has been almost entirely replaced by copper, thereby greatly diminishing the cost. A current of 50 volts and 15 amperes gives a liter of the gas in twelve minutes, so that the preparation of fluorine has become an easy lecture-table experiment. The next chapters are upon the physical properties of the element, its action upon metals and non-metals and their compounds and a study of the products. Its action on organic substances and its organic compounds are next studied, and the final chapter deals with some of the constants and recently discovered properties of the element. The bibliography is double, chronological and alphabetical, and contains more than 570 titles. It is impossible in a review to mention even a small fraction of the important and interesting experiments described in the book. We learn that the color of fluorine is greenish-yellow, lighter and more yellowish than that of chlorine. It boils at —187° and is still active at that temperature. At —210°, though without action on water or mercury, it combines violently with hydrogen or turpentine. Many metallic fluorides resemble the oxides, but the relationship between non-metallic fluorides and chlorides is so intimate that the element clearly belongs in the chlorine family. As fluorine, deprived of hydrofluoric acid by cooling, does not attack glass, pure fluorine is easily handled in ordinary apparatus. The discovery of this fact opens a new field of investigation, in which work has begun. Little is said of the compounds of fluorine and sulphur, their study apparently coming after the completion of the book. On the whole, it may be said that the book is one that should be read carefully by every student of chemistry, for it is a model of clearness, as the work it describes is a triumph of vigorous experimentation.

FELIX LENGFELD.

DIE WISSENSCHAFTLICHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. Von W. OSTWALD. Dritte vermehrte Auflage. Leipzig: W. Engelmann. 1901. 220 pp.

The value of this book and its important bearing on the theoretical side of analytical chemistry have already been noted in the reviews of previous editions. This enlarged edition was called forth by the recent rapid advance in the methods of elementary instruction advocated by the author, methods which he says have been adopted in a number of the larger institutions and whose general use he thinks will only be a matter of time. He has added an appendix containing a number of experiments suitable for lecture demonstrations on the principles of analytical chemistry as taught in the book. The author, by this means, hopes also to arouse others to activity in this interesting and productive field.

J. E. G.

EXPERIMENTS FOR STUDENTS IN GENERAL CHEMISTRY. BY EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania, and HARRY F. KELLER, Professor of Chemistry, Central High School of Philadelphia. Fourth edition, enlarged. Philadelphia: P. Blakiston's Son & Co. 1900. 80 pp. Price, 60 cents.

This book is intended as a laboratory guide to be used with a reference book, and is a collection of experiments from various sources. The experiments are well chosen and arranged in logical order of complexity with a number of problems upon the weight and volume relations of reactions. The student is taught to observe carefully the different stages of the reactions, and must consult reference books in connection with the experiments. The book can be recommended for use in colleges and high schools when a general course in inorganic chemistry is offered, and in case a full course is not possible a selection of typical experiments could readily be made by the teacher. J. E. G.

QUALITATIVE CHEMICAL ANALYSIS, ORGANIC AND INORGANIC. By F. M. PERKIN, PH.D., Head of the Chemistry Department, Borough Polytechnic Institute, London. London: Longmans, Green & Co. 1900. 260 pp.

The author remarks in his preface that, recognizing the difference between book students and laboratory students, he has endeavored to write a book in which theory and practice are more or less dovetailed. He has, however, only introduced sufficient theory to make it practical and at the same time clear and interesting. In the main, the inorganic part is similar to that of other works of this kind except that he has introduced the reactions in most cases and some of the recent ideas of the nature of solutions in order to explain the reactions of analytical chemistry. The author does not make this the important feature, but gives only an outline sketch of the general principles to enable the student to grasp the nature of ions and their action in solutions. He also gives in many cases several methods for the separation of the members of the different groups. In the organic part he gives some of the reactions and methods of separation of the different groups and calls attention to the impossibility of giving a general method for the separation of organic compounds on account of their great number and the variation in their properties caused by the presence of different groups. This book might be regarded as intermediate between the very brief courses in analysis and the very complete ones which serve as reference books rather than as practical guides to analyses. It is well printed and generally attractive. J. E. G.

QUALITATIVE CHEMICAL ANALYSIS. A guide in qualitative work with data for analytical operations and laboratory methods in inorganic chemistry. By ALBERT B. PRESCOTT and OTIS C. JOHNSON, Professors in the University of Michigan. Fifth revised and enlarged edition, entirely rewritten. New York: D. Van Nostrand Co. 1901. pp. 420. $3.50 net.

In the preface the authors state that "the text has been rewritten and the order of statement in good part recast. The subject-matter is enlarged by fully one-half, though but 100 pages have been added to the book." "It has been our aim to bring the varied resources of analysis within reach, placing in order before the worker the leading characteristics of elements, upon the relations of which every scheme of separation depends. This is desired for the working chemist and no less for the working student. However limited may be the range of his work, we would not contract his view to a single routine. It is while in the course of qualitative analysis especially that the student is forming his personal acquaintance with the facts of chemical change, and it is not well that his outlook should be cut off by narrow routine at this time."

They have, at the request of teachers, introduced in a revised form the portion upon operations of analysis, which contains some of the foundations of qualitative chemistry, and which was omitted in the last edition. They have also devoted four pages to an outline sketch of the principles of solutions and ionization, and several pages to a general discussion of the periodic system.

Part II. contains the chemistry of the metals, Part III., that of the non-metals, and Part IV., directions for systematic examinations and methods of special treatments, tables, equations, problems in synthesis and the preparation of reagents.

In the portion devoted to the chemistry of the metals, the metals and their compounds are treated in a very thorough manner, the occurrence given, and all the possible reactions discussed and the composition of the compounds formed given, with the equations, in many cases, representing the reaction.

One of the very valuable features is the introduction of the references to the original authorities in the journals. Not only methods of detection, but also methods of estimating the substance by gravimetric and volumetric methods are given. In the directions for separating the groups and members of groups, very complete notes are given, covering the possible difficulties which may arise. The amount of space, 238 large pages, of which at least half consists of small type, devoted to the metals and their compounds, will convey some idea of the amount of material contained in this book, especially when we consider the very condensed form of the statements. About 120 pages are devoted to the non-metals, especially the acids, when the properties, occurrence, formation, preparation, solubility, reactions, detection, and estimation are discussed.

This book contains material which can perhaps be found in no single text-book, and which, in a condensed form, contains much of the material found in the dictionaries of chemistry. It is a very valuable reference book, both for students of advanced inorganic chemistry and teachers, and a copy should be in every chemical library and accessible to every student. The authors are to be congratulated upon the success of the book, as evidenced by the number of editions, the clear and systematic method of presentation and the collection of reactions, which it is often impossible for a student to find explained in a satisfactory and simple manner. J. E. G.

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CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Cornell University.

THE CONSTITUTION OF GALLEÏN AND COERULEÏN.[1]

By W. R. Orndorff and C. E. Brewer.

I. GALLEÏN.

Galleïn was discovered by A. von Baeyer[2] in 1871. He made it by heating together phthalic anhydride and pyrogallol and, at first, regarded it as derived from pyrogallol by the loss of water according to the reaction

$$3C_6H_6O_3 = C_{18}H_{14}O_7 + 2H_2O.$$

Pyrogallol. Galleïn.

Later[3] he tried the action of phthalic anhydride on other phenols and found that they reacted in a similar manner. To the compounds resulting he gave the name phthaleïns, as he found that the phthalic anhydride took part in the reaction. From the analysis of phenolphthaleïn he concluded that it was made up of one residue of phthalic anhydride and two of phenol and represented the reaction thus:

$$C_8H_4O_3 + 2C_6H_6O = C_{20}H_{14}O_4 + H_2O.$$

Phthalic anhydride. Phenol. Phenolphthaleïn.

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[1] For the preliminary article on this subject see this Journal, 23, 425.

[2] Ber. d. chem. Ges., 4, 457.

[3] *Ibid.*, 4, 658.

Resorcinphthaleïn, or fluoresceïn, he regarded as a double anhydride, representing the reaction as follows:

$$\underset{\text{Phthalic anhydride.}}{C_8H_4O_3} + \underset{\text{Resorcin.}}{2C_6H_6O_2} = \underset{\text{Fluoresceïn.}}{C_{20}H_{12}O_5} + 2H_2O.$$

The study of these reactions probably led him to change his views regarding the formation of galleïn, for in this article it is considered to be the phthaleïn of pyrogallol, being formed in accordance with the following equation:

$$\underset{\text{Phthalic anhydride.}}{C_8H_4O_3} + \underset{\text{Pyrogallol.}}{2C_6H_6O_3} = \underset{\text{Galleïn.}}{C_{20}H_{12}O_7} + 2H_2O.$$

The formula given for galleïn in the first paper, $C_{18}H_{14}O_7$, was found to be incorrect, owing to the property of the substance of forming a crystallized compound with alcohol. By purifying the galleïn without the use of alcohol, a product was obtained which gave, on analysis, results agreeing with the formula $C_{20}H_{12}O_7$. This view of the constitution of galleïn, that it is made up of two residues of pyrogallol combined with one of phthalic anhydride, he confirmed by showing that, on oxidation with nitric acid, galleïn yields, besides oxalic acid, phthalic acid in considerable quantity.

When the phthaleïns in alkaline solution are reduced with zinc dust, Baeyer found that the solution was almost immediately decolorized and that the phthaleïns were converted into their leuco compounds, which he designated *phthalins*. For phenolphthalin he determined the formula to be $C_{20}H_{16}O_4$, while to gallin, the phthalin of galleïn, he gave the formula $C_{20}H_{18}O_7$.

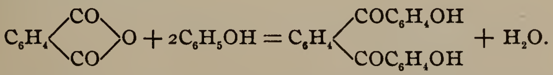
In this second paper on phenol dyes Baeyer suggests that phenolphthaleïn is formed in an analogous manner to sulphobenzid from benzene and sulphuric anhydride, as shown in the following equations:

$$\underset{\text{Phthalic anhydride.}}{C_8H_4O_3} + \underset{\text{Phenol.}}{2C_6H_6O} = \underset{\text{Phenolphthaleïn.}}{C_{20}H_{14}O_4} + H_2O;$$

$$\underset{\text{Sulphuric anhydride.}}{SO_3} + \underset{\text{Benzene.}}{2C_6H_6} = \underset{\text{Sulphobenzid.}}{C_6H_5SO_2C_6H_5} + H_2O.$$

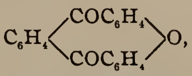
He adds, however, the following words, which are extremely interesting in view of the later conceptions of the constitution of the phthaleïns: "Wenn dieser Vorgang vielleicht dabei auch stattfindet, so ist er doch aller Wahrscheinlichkeit nach nicht der einzige, weil das Phthaleïn sich in Kalilauge mit prachtvoller Fuchsinfarbe löst und durch Zinkstaub in alkalischer Lösung entfärbt wird. Nach obiger Formel könnte diese Erscheinung nur durch das Verhalten der Acetongruppe hervorgerufen werden; nach den bisherigen Erfahrungen ist es aber wahrscheinlicher, das eine chinonartige Gruppe dazu Veranlassung giebt."

Fuoresceïn, on account of the beautiful fluorescence of its alkaline solutions and the fact that it is a yellow dyestuff, was the first of the phthaleïns to be closely investigated, and it is interesting to note in this connection that Emil Fischer's inaugural dissertation, published at Strassburg in 1874, was on fluoresceïn and orcinphthaleïn. In 1876 Baeyer published the first detailed account[1] of his investigations on the compounds of phthalic acid with the phenols. The reaction between phthalic anhydride and phenol he represents by the following equation:



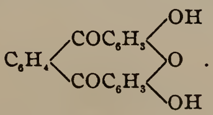
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + 2C_6H_5OH = C_6H_4\left\langle\begin{matrix}COC_6H_4OH\\COC_6H_4OH\end{matrix}\right. + H_2O.$$

Fluoresceïn he regards as belonging to the group of the phthaleïn anhydrides, whose simplest representative is phenolphthaleïn anhydride,



$$C_6H_4\left\langle\begin{matrix}COC_6H_4\\COC_6H_4\end{matrix}\right\rangle O,$$

formed as a by-product in the preparation of phenolphthaleïn. The constitution of fluoresceïn must then, according to Baeyer, be expressed by the following formula:



$$\begin{array}{lll} & & OH \\ & COC_6H_3\langle & \\ C_6H_4\langle & & \rangle O \\ & COC_6H_3\langle & \\ & & OH \end{array}.$$

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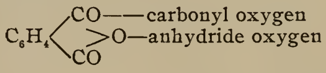
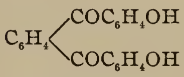
[1] Ann. Chem. (Liebig), 183, 2.

In his second detailed paper[1] on the phthaleïns, published in 1880, Baeyer modified his views of the structure of these compounds very materially. In studying the action of fused caustic potash on phenolphthaleïn he found that one of the products was dioxybenzophenone. According to the diketone formula for phenolphthaleïn, the formation of dioxybenzophenone could only be explained by assuming a shifting of one of the phenol residues. If, however, we suppose that, in the formation of the phthaleïn, it is the carbonyl and not the anhydride oxygen, which is replaced by the two phenol residues, then the formation of dioxybenzophenone follows as a matter of course, as will be readily seen from the following formulas and equation :

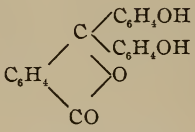


$$C_6H_4\begin{cases}CO\text{——carbonyl oxygen}\\ CO\end{cases}\!\!>O\text{—anhydride oxygen}$$

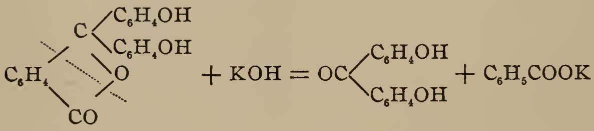


$$C_6H_4\begin{cases}COC_6H_4OH\\ COC_6H_4OH\end{cases}$$

Phenolphthaleïn.
(Diketone formula.)

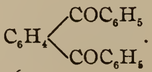


Phenolphthaleïn.
(New formula.)



Phenolphthaleïn. Dioxybenzophenone.

Further evidence in favor of the new formula for phenolphthaleïn was found in studying the phthalophenone of Friedel and Crafts. To this substance, made by the action of phthalyl chloride on benzene in the presence of aluminium chloride, had been assigned the following formula by the above-named authors :



$$C_6H_4\begin{cases}COC_6H_5\\ COC_6H_5\end{cases}.$$

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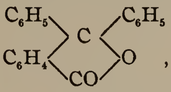
[1] Ann. Chem. (Liebig), 202, 36.

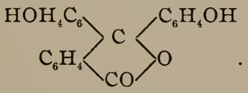
Baeyer found that it is in reality diphenylphthalid,



as it gave, on reduction in alkaline solution with zinc, triphenylmethanecarbonic acid,

$$C\left\{\begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_4COOH, \\ H \end{array}\right.$$

which, when heated with barium hydroxide, splits up into triphenylmethane and carbon dioxide. This same diphenylphthalid was converted into dinitrodiphenylphthalid by the action of nitric acid; on reduction, this gave diamidodiphenylphthalid, which with nitrous acid and water yielded dioxydiphenylphthalid, identical in every respect with phenolphthaleïn. The formula for phenolphthaleïn must hence be:

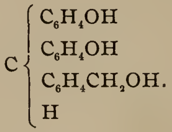


The position of the hydroxyl groups with reference to the methane carbon atom was assumed by Baeyer to be para, because substances in which the para position is occupied, such as parachlorphenol and paracresol, do not give phthaleïns, but phthaleïn anhydrides, while the ortho-substituted phenols give phthaleïns with the greatest ease. The formation of paradioxybenzophenone, when phenolphthaleïn is fused with caustic potash, is also in accord with this assumption.

To phenolphthalin, the product obtained from phenolphthaleïn by reduction in alkaline solution with zinc, Baeyer gives the formula

$$C\left\{\begin{array}{l} C_6H_4OH \\ C_6H_4OH \\ C_6H_4COOH, \\ H \end{array}\right.$$

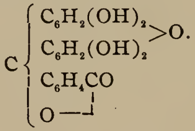
while phthalol, the product resulting from the phthalin by reduction in acetic acid solution with sodium amalgam, he represents as follows:



$$C\left\{\begin{array}{l} C_6H_4OH \\ C_6H_4OH \\ C_6H_4CH_2OH. \\ H \end{array}\right.$$

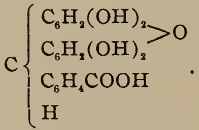
Gallin, the reduction-product of galleïn, corresponds, according to him, to this phthalol.

In 1881 K. Buchka[1] published his investigations on galleïn and coeruleïn. According to Buchka, Baeyer regarded galleïn, $C_{20}H_{12}O_7$, as a phthaleïn anhydride analogous to fluoresceïn, which it closely resembles. The following formula would therefore express its constitution:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O. \\ C_6H_4CO \\ O \text{—┘} \end{array}\right.$$

The formation of a tetracetate and a tetrabenzoate, indicating the presence of four hydroxyl groups in galleïn, is only an apparent confirmation of this formula, according to Buchka, as it is not possible to explain by it the conduct of galleïn toward reducing agents. Galleïn takes up 2 atoms of hydrogen when treated in alkaline solution with zinc dust, and if it had the above constitution it could only give a compound corresponding to phenolphthalin and having the following formula:



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right> O \\ C_6H_4COOH \\ H \end{array}\right. .$$

A compound of this structure, however, must possess acid properties and yield, when treated with concentrated sulphuric acid, a product corresponding to phenolphthalidin. But galleïn, reduced in the cold according to Buchka, does not have acid properties and, though the reduced product dissolves in cold concentrated sulphuric acid, it is precipitated out again unchanged on the addition of water. By further reduction, however, this reduced product takes up two more atoms of hydrogen and is converted into a compound, which reacts strongly acid and is converted by sulphuric acid, even in the cold, into coerulin, corresponding to phenolphthalidin. This second reduction-product of galleïn must, therefore, according to Buchka, have a constitution corresponding to phenolphthalin and hence he calls it gallin. Buchka then took up the question as to the constitution of the substance intermediate between galleïn and gallin. He found that galleïn, reduced in alkaline solution in the cold with zinc dust, gave with acetic anhydride an acetate identical in all respects with the tetracetyl galleïn made from galleïn by heating it with acetic anhydride and sodium acetate. This remarkable result led him to assume that galleïn can take up 2 atoms of hydrogen without affecting the phthalic anhydride residue and that this hydrogen adds itself, in some way, to the two pyrogallol residues, which must be supposed to have suffered a partial oxidation in the preparation of galleïn. By assuming that in the formation of galleïn two of the hydroxyl groups belonging to the pyrogallol residues form a quinone group in a way analogous to the formation of cedriret,

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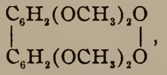
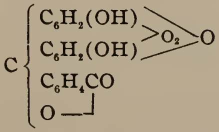
[1] Ann. Chem. (Liebig), 209, 251.



$$\begin{array}{l} C_6H_2(OCH_3)_2O \\ \vert \qquad\qquad\quad \vert \\ C_6H_2(OCH_3)_2O \end{array},$$

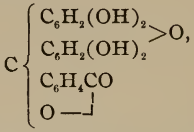
by the oxidation of the dimethyl ether of pyrogallol, he arrives at the following formula for galleïn :



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH) \\ C_6H_2(OH) \end{array}\right> O_2 > O \\ C_6H_4CO \\ O \text{—┘} \end{array}\right.$$

Galleïn according to Buchka.

When reduced in the cold, a compound of this formula would, according to him, take up 2 atoms of hydrogen, the quinone group being first reduced, and the product formed, which he calls hydrogalleïn,

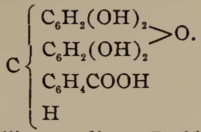


$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{array}\right>O,\\C_6H_4CO\\O-\!\!\rfloor\end{array}\right.$$

Hydrogalleïn, according to Buchka.

would not have the character of an acid nor could it be converted by the action of sulphuric acid into a phthalidin. On the other hand, this compound would give a tetracetyl derivative. He states that the formation of this same tetracetyl product from galleïn itself might be regarded as an argument against the assumption of a quinone group in galleïn, since we should naturally expect here the formation of only a diacetyl galleïn. The analyses of both products, however, proved the presence of four acetyl groups and, moreover, the properties of this galleïn tetracetate do not accord with the assumption of the presence of a quinone group. We must, therefore, according to him, if we hold to the assumption of a quinone bond or union in galleïn, suppose a breaking of this union in the formation of the tetracetyl galleïn. Quinone, and chloranil act in an analogous manner. Thus Sarauw obtained diacetyl hydroquinone by the action of acetic anhydride and sodium acetate on quinone and Graebe made diacetyltetrachlorhydroquinone by heating chloranil with acetyl chloride. The quinone union may therefore be broken by an acid anhydride or an acid chloride, though with difficulty, and the taking up of four acid residues in the formation of tetracetyl galleïn is not contrary to the assumption of a quinone group in galleïn. From this reasoning Buchka concludes that galleïn does not have the formula $C_{20}H_{12}O_7$, last assigned to it by Baeyer, but one containing 2 atoms of hydrogen less, $C_{20}H_{10}O_7$.

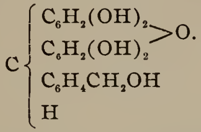
On further reduction of the hydrogalleïn, $C_{20}H_{12}O_7$, there is formed the compound corresponding to phenolphthalin:



$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{array}\right> O.\\C_6H_4COOH\\H\end{array}\right.$$

Gallin, according to Buchka.

This compound Buchka calls gallin, a name which Baeyer originally gave to the last reduction-product of galleïn, corresponding to phthalol, which Buchka designates gallol. To this gallol he assigns the formula

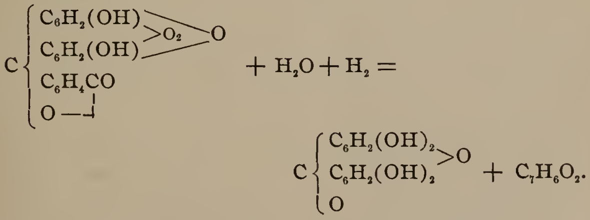


$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{array}\right> O.\\C_6H_4CH_2OH\\H\end{array}\right.$$

Gallol, according to Buchka.

Gallin, he found to give with acetic anhydride a tetracetyl, and gallol a pentacetyl, derivative.

By fusing with alkalies, Buchka found that galleïn is split up in an analogous manner to phenolphthaleïn. It gives, besides benzoic acid, the anhydride of pyrogallol ketone by taking up 2 atoms of hydrogen. He represents the reaction as follows:



$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_2(OH)\\C_6H_2(OH)\end{array}\right> O_2 > O\\C_6H_4CO\\O\text{ —┘}\end{array}\right. + H_2O + H_2 =$$

$$C\left\{\begin{array}{l}\left.\begin{array}{l}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{array}\right> O\\O\end{array}\right. + C_7H_6O_2.$$

In 1892 Herzig[1] repeated a part of Buchka's work on galleïn and obtained results which do not agree with those given by Buchka. The formation of colorless acetyl derivatives of quercetin and ethyl quercetin, etc., made it appear possible to Herzig that these colorless products were not acetyl derivatives of the original dyestuffs, but of their leuco compounds, especially since Graebe and Caro[1] had already obtained, by the action of acetic anhydride on rosolic acid, not acetyl rosolic acid but the acetyl derivative of leucorosolic acid. The melting-points of acetyl phenolphthaleïn and acetyl phenolphthalin, as given by Baeyer (143° and 146°), are very nearly the same, and preliminary experiments showed that acetyl fluoresceïn and acetyl fluorescin melted at practically the same point (200° to 201° and 200° to 202°). This suggested to Herzig the idea that phenolphthaleïn and fluoresceïn give with acetic anhydride acetyl phenolphthalin and acetyl fluorescin, reduction as well as acetylization taking place. This idea did not prove correct, however, for while acetyl fluoresceïn and acetyl fluorescin have the same melting-point they differ very markedly in their conduct towards dilute alkali solutions. Acetyl fluoresceïn dissolves in dilute alkalies only in so far as it is saponified and even after some hours undissolved acetyl fluoresceïn may be regained by filtration. Acetyl fluorescin, on the other hand, dissolves very readily in dilute alkalies in the cold and if the solution is quickly acidified it may be regained unsaponified with the melting-point 200° to 202°. The same difference is shown by acetyl phenolphthaleïn and acetyl phenolphthalin and is a necessary consequence of the constitution of the phthaleïn and phthalin.

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[1] Monatsh Chem., 13, 425.

Herzig then calls attention to the fact that Buchka claims to have obtained, by reduction, a product, hydrogalleïn, intermediate between galleïn and gallin. Acetyl gallin he found to be an acid, and hence gallin bears the same relation to galleïn that fluorescin does to fluoresceïn. Hydrogalleïn, however, is said to yield the same acetyl product as galleïn itself, and from this fact Buchka concludes that two quinone-oxygen atoms are present in galleïn. Owing to the importance of this observation for the constitution of galleïn and that Buchka does not describe the conduct of the two acetyl products towards dilute alkalies, Herzig thought it advisable to repeat this part of Buchka's work. He first made tetracetyl galleïn and found that it melted, when recrystallized from benzene, at 234° to 237°. Buchka gives it the melting-point 247° to 248°. This difference caused Herzig to repeat the preparation of his acetyl galleïn. He obtained a product with the same melting-point, 236° to 237°. From this acetyl galleïn he made pure galleïn by saponification. This he reduced with caustic potash and zinc dust in the cold exactly as Buchka directs. The product had the appearance and properties of hydrogalleïn but it gave with acetic anhydride not acetyl galleïn but a substance which, when recrystallized from benzene, melted at 210° to 213°. Moreover, it differed from acetyl galleïn soluble in caustic alkali without saponification, which is naturally not the case with acetyl galleïn. This product Herzig assumes to be the tetracetyl gallin, which, according to Buchka, melts at 220°. Owing to this difference in melting-point, Herzig repeated the reduction experiment, avoiding all heating and working so that the entire reaction was ended in a quarter of an hour. Notwithstanding all these precautions, however, the product had the same melting-point (211° to 213°). Herzig concludes his article with the following words: "Buchka scheint nach seiner Beschreibung eine grössere Menge des Hydrogalleïns in der Hand gehabt zu haben, und es können daher meine beiden negativen Befunde vorläufig die Existenz desselben nicht in Frage stellen. Allerdings glaube ich, dass die Darstellung des Hydrogalleïns nicht so einfach ist, wie sie Buchka beschreibt und dass noch andere Vorsichtsmassregeln nothwendig sind, die der genannte Autor entweder nur unbewusst eingehalten oder in seiner Arbeit zu erwähnen vergessen hat. Ebenso halte ich es vorläufig nicht für ausgeschlossen, dass die Identität der Acetylproducte des Galleïns und Hydrogalleïns nur auf Grund der Schmelzpunkte ausgesprochen wurde, während sie sich in Bezug auf die Löslichkeit in Alkalien von einander so unterscheiden können, wie Acetylfluoresceïn von Acetylfluorescin."

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[1] Ann. Chem. (Liebig), 179, 198.

For some years previous to this date (1892) the views of chemists as to the chemical nature of colored organic compounds, the cause of their color, and the relation of this physsical property to their chemical constitution had undergone important changes.[1] These colored compounds, which had been considered as derivatives of benzene and related hydrocarbons, were coming more and more to be regarded as derivatives of the dihydro addition-products of these hydrocarbons; *i. e.*, as quinone-like compounds or as having a quinoid structure, the quinones themselves being considered as para- or orthodiketones.

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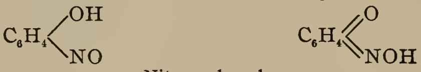
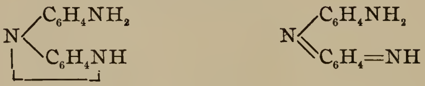
[1] See in this connection H. E. Armstrong's paper "On the Origin of Color." Proc. Chem. Soc., 1887–1888, No. 49, p. 27.

The relation between the old and the new ideas regarding the constitution of colored organic compounds will be readily seen from the following formulas:

Old formula. New (quinoid) formula.



Nitrosophenols.



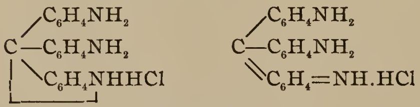
Indamine.

$C_6H_5N_2C_6H_4OH$ $C_6H_5NHN{=}C_6H_4{=}O$

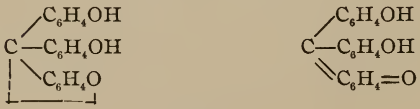
Oxyazobenzene.

$C_6H_5N_2C_6H_4NH_2$ $C_6H_5NH.N{=}C_6H_4{=}NH$

Amidoazobenzene.



Pararosaniline hydrochloride.



Aurin.

In 1892 A. Bernthsen[1] put forward certain very interesting and important speculations as to the structure of the phthaleïns in an address before the Chemical Society at Heidelberg on the constitution of the rhodamines and eosines.

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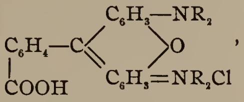
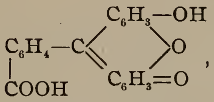
[1] Chem. Ztg., 104, 1956 (1892).

After proving that the constitution of rhodamine hydrochloride is correctly represented by the formula



Rhodamine hydrochloride.

he assumes an analogous constitution for the corresponding hydroxyl dyes; for example, he gives fluoresceïn in its salts the formula

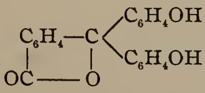


Fluoresceïn in its salts.

while for the free fluoresceïn, which yields a diacetyl product, the lactone formula of Baeyer is retained. The fact that fluoresceïn gives an easily saponifiable ethyl derivative (an ester), which may also be made by oxidation of the colorless fluorescin ethyl ester, is the chief argument in favor of the above formula.

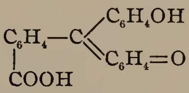
It is very probable also, according to Bernthsen, that the characteristic color change of phenolphthaleïn with an alkali is to be explained by assuming that the colorless compound has the lactone formula (I.), but in the violet-red salts the quinoid formula (II.):

I.



Phenolphthaleïn.

II.

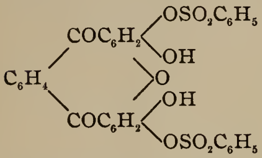


Phenolphthaleïn in its salts.

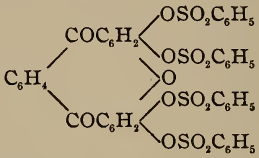
Since the publication of this address of Bernthsen, much work has been done on the phthaleïns with a view to determining their constitution. The phthaleïns are now generally regarded as tautomeric substances, since they yield both colorless and colored derivatives. The colorless compounds are given the lactoid[1] structure, while the colored products are considered to be quinoid derivatives.

While much work has been done on phenolphthaleïn and fluoresceïn and their constitution has been fully determined, galleïn has been neglected since Buchka published the results of his investigations.

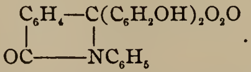
M. Georgescu[2] has made the dibenzene- and tetrabenzenesulphonates by treating alkaline solutions of galleïn with benzene sulphonchloride and given them the formulas



and

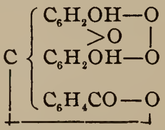


and Albert[3] the galleïn anilide by heating galleïn with aniline and aniline hydrochloride. He describes it as a colorless compound, soluble in alkalies without color, and gives it the formula



$$\begin{array}{l} C_6H_4{-}C(C_6H_2OH)_2O_2O \\ \;|\qquad\quad | \\ OC{-\!-\!-}NC_6H_5 \end{array} \;.$$

From this anilide he made what he calls a dimethyl ether, also colorless, by heating it with methyl iodide in a sealed tube to 100°. Schultz and Julius, in their "Tabellarische Uebersicht der künstlichen organischen Farbstoffe" (edition of 1891, page 98), give galleïn the following formula :



$$C\begin{cases} C_6H_2OH{-}O \\ \qquad >O \quad | \\ C_6H_2OH{-}O \\ \\ C_6H_4CO{-}O \end{cases}$$

The same structure is given to it in Léon Lefèvres' "Matières Colorantes Artificielles'' (1896, page 1190). Nietzki, in his ''Chemie der organischen Farbstoffe'' (1897), gives it the structure :

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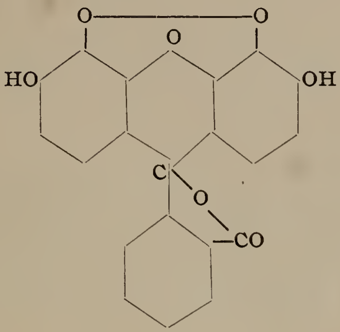
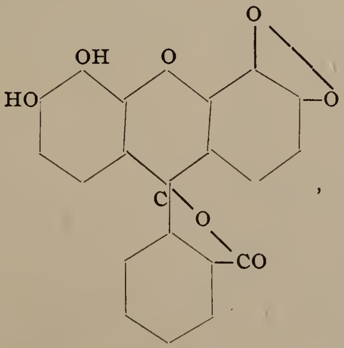
[1] We have adopted the term lactoid instead of lactone. It is more comprehensive and may be used to designate compounds like the anilides and hydrazides of the phthaleïns which are not lactones.

[2] Buletinul Societatii de Sciinte Fizice d. Bucuresci Romania, 1, 215 (1892).

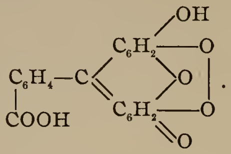
[3] Ber. d. chem. Ges. 26, 3077.



He adds, however: ''Wahrscheinlich ist es fast, dass diese beiden Sauerstoffatome in einem Kern eine Orthochinongruppe bilden, auch dürfte das Galleïn zu den chinoïden Carboxylderivaten gehören.'' Schultz and Julius, in the 1897 edition of their book, page 142, give its structure as follows, representing it as an orthoquinone,



while Krafft in his "Organische Chemie," 1897, page 595, follows the other suggestion of Nietzki and gives it the structure



II. COERULEÏN.

This compound was also discovered by Baeyer[1] in 1871. He made it by heating galleïn with 20 parts of concentrated sulphuric acid to 200° and precipitating the product with water. From the analysis of the substance he deduced the formula $C_{18}H_{10}O_6$ and represented its formation from galleïn by the following equation :

$$\underset{\text{Galleïn.}}{C_{18}H_{14}O_7}-H_2O-H_2=\underset{\text{Coeruleïn.}}{C_{18}H_{10}O_6}.$$

He found that the coeruleïn was reduced to a compound, which he called coerulin, by the action of ammonia and zinc dust. This same coerulin was also obtained from the reduction-product of galleïn, gallin, by gently heating it with concentrated sulphuric acid. In a later paper,[2] after he had determined the correct formula for galleïn to be $C_{20}H_{12}O_7$, he finds that coeruleïn has the formula $C_{20}H_{10}O_7$ and gives the following series :

Gallin, $C_{20}H_{18}O_7$;
Galleïn, $C_{20}H_{12}O_7$;
Coeruleïn, $C_{20}H_{10}O_7$.

Though coeruleïn was the first of the class of compounds, which Baeyer[3] called phthalideïns, to be discovered, its structure was not investigated until after that of phenolphthalideïn had been determined. This phenolphthalideïn was made by the oxidation of phenolphthalidin, resulting from the action of sulphuric acid on phenolphthalin. This phenolphthalidin Baeyer regards as dioxyphenylanthranol, and represents the reaction by which it is formed as follows:

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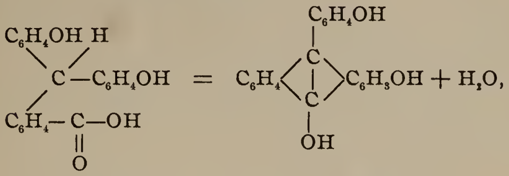
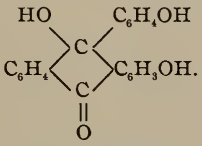
[1] Ber. d. chem. Ges., 4, 556.
[2] *Ibid.*, 4, 663.
[3] Ann. Chem. (Liebig), 202, 90.



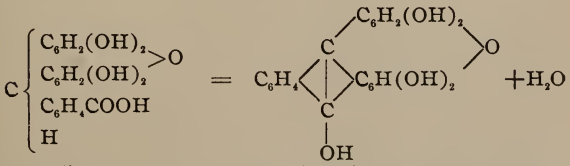
Phenolphthalin. Phenolphthalidin.

since it results from the phthalin by the loss of one molecule of water, and may be converted into the phthalin by superheating with water. Phenolphthalideïn, formed by the oxidation of the phthalidin, he regards as dioxyphenyloxanthranol,



Phenolphthalideïn.

In 1881 Buchka[1] took up the study of coeruleïn and coerulin in connection with his work on galleïn. He found that coerulin is formed from gallin by the action of concentrated sulphuric acid in the same manner as phenolphthalidin from phenolphthalin and represents the reaction by the following equation:



Gallin. Coerulin.

From this coerulin he made what he terms the tetracetyl ether by the action of acetic anhydride. He explains the formation of this compound by assuming that the hydroxyl group, joined to the γ-carbon atom, does not react with acetic anhydride. On oxidation of this coerulin it goes over into coeruleïn, which may also be formed directly from galleïn by heating with concentrated sulphuric acid. Hence, according to Buchka, coeruleïn also contains a quinone group, and if it were analogously constituted to phenolphthalideïn, it would have the formula

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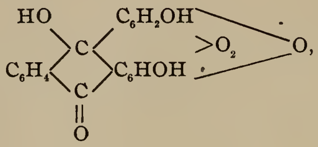
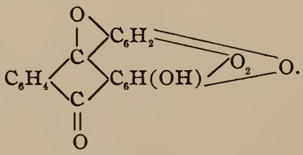
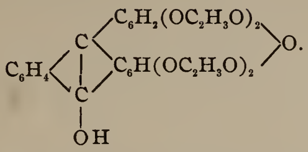
[1] Ann. Chem. (Liebig), 209, 258 and 272.



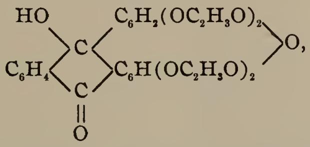
and, on treatment with acetic anhydride, it should give a tetracetyl ether, owing to the reduction of the quinone group; but it gives a red-colored triacetyl ether. In order to explain the formation of this compound, Buchka assumes that the quinone bond in coeruleïn is broken by the action of the acetic anhydride as it is in galleïn, but that the hydroxyl group of the γ-carbon atom then unites with one of the pyrogallol residues with the separation of water and formation of a condition like that in rosolic acid. Thus he arrives at the following formula for coeruleïn :



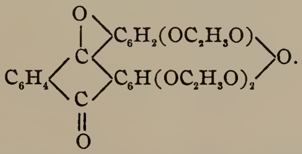
This formula is shown to be correct, he thinks, by the fact that the triacetyl coeruleïn may also be made by the oxidation of the tetracetylcoerulin, which undoubtedly has the formula



This substance could give, on oxidation, a product containing a quinone group by the separation of two acetyl residues, thus forming a diacetyl coeruleïn. It cannot yield, however, a triacetyl ether containing a quinone group. He explains the formation of triacetyl coeruleïn by assuming that the tetracetyl coerulin forms, on oxidation, a tetracetyl coeruleïn, perhaps of this structure,



which, as soon as formed, splits off a molecule of acetic acid and goes over into a triacetyl coeruleïn of the formula



On heating with zinc dust, coeruleïn yields phenylanthracene, according to Buchka, thus showing that it is a derivative of this hydrocarbon.

In 1894 M. Prud'homme[1] published a short article on the constitution of coeruleïn. He states that the substance condenses with 2 molecules of aniline, with the loss of 2 molecules of water, to form a new dye. This new substance does not form lakes with iron, chromium, or aluminium mordants, and hence, he thinks, no longer contains any hydroxyl groups.

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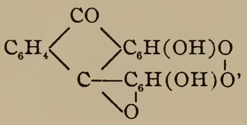
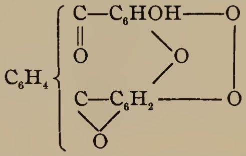
[1] Bull. soc. chim. (Paris), (3), 11, 1136.

The formation of the new compound from coeruleïn depends upon the hydroxyl groups, and as the coeruleïn had the power of combining with 2 molecules of aniline it must contain two hydroxyl groups. This assumption of the presence of two hydroxyl groups in the molecule of coeruleïn is also, according to Prud'homme, in harmony with the law of Liebermann and Kantanecki, that only those oxyketone dyes in which two hydroxyl groups are in the ortho position, act as mordant dyes. He therefore gives the following formula to coeruleïn,

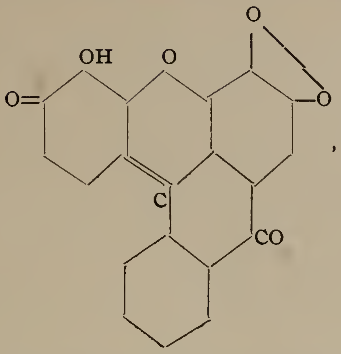


which represents it as containing two hydroxyl groups and as a derivative of phenyloxanthranol.

In Schultz and Julius' "Tabellarische Uebersicht der künstlichen organischen Farbstoffe," edition of 1891, page 98, the following formula is given for coeruleïn:



Nietzki, in his "Chemie der organischen Farbstoffe" (1897), page 175, gives it the same formula, but adds in a foot-note the following remark: "Eine Controlle dieser Formel wäre wohl zeitgemäss. Die vielen Sauerstoffbindungen lassen sich kaum mit den heutigen Anschauungen über derartige ringförmig constituirte Molecule vereinigen. Auch sind die beizenfärbenden Eigenschaften bei Vorhandensein nur einer Hydroxylgruppe kaum zu erklären." In the 1897 edition of their work, page 142, Schultz and Julius give the following formula to coeruleïn,



representing it as a quinoid dyestuff containing also an orthoquinone group.

From the foregoing historical review may be gathered the development of ideas in regard to the structure of the phthaleïns and phthalideïns down to the present time. In the following pages is given an account of an investigation undertaken with a view to throwing additional light upon the subject so far as two of these are concerned—galleïn and coeruleïn.

EXPERIMENTAL.

I. GALLEÏN.

The galleïn used in this investigation was supplied by the Badische Anilin und Soda Fabrik, Ludwigshafen-am-Rhein, to whom grateful thanks are herewith tendered for the generous interest they have manifested in the work. It was an unusually pure product and beautifully crystallized. By transmitted light it was red; by reflected light, under the microscope, greenish-yellow with a metallic luster. When seen in bulk it has a decided green color. When acetylized it left no residue other than galleïn acetate.

Galleïn dissolves in an aqueous solution of pyrogallol, more easily in boiling solution, from which, after several hours, it crystallizes out. That galleïn, in addition to its marked acid properties, has slight basic properties, is shown by the fact that its solubility in water or alcohol is considerably increased by the presence of an acid. This same conduct on the part of fluoresceïn was noted by Baeyer[1] and by Waddell.[2] In the case of aurin, which resembles galleïn to a marked degree, Dale and Schorlemmer[3] have isolated a hydrochloric acid salt.[4]

When galleïn is dissolved in alcohol and an alcoholic solution of potassium hydroxide in excess is added, the potassium salt of galleïn is precipitated. It has a blue color and probably contains 4 atoms of potassium.

Attempts were made to reduce galleïn by means of hydrogen sulphide. Solutions in ammonium hydroxide, in potassium hydroxide, sodium carbonate, and in alcohol remained unchanged after passing the gas through them for some time. Sulphur dioxide was also tried as a reducing agent, but with negative results. An alcoholic solution of galleïn remains unchanged when treated with sulphur dioxide. Galleïn in dilute caustic potash solution, when treated with sulphur dioxide, is thrown down as a dark-red precipitate, due to the neutralization of the potassium hydroxide.

An aqueous solution of galleïn, made by boiling galleïn with water and filtering the solution, when treated with a solution of lead acetate or lead nitrate in water, gives first a deep-blue solution from which, finally, all the galleïn is precipitated as the basic lead salt, with indigo-blue color. This reaction is quite delicate and might be used as a test for either galleïn or lead. Gallein does not melt or undergo any change when heated to 300° C.

Air passed through a solution of galleïn in caustic potash solution causes the color to change from deep-blue to brown. Hydrochloric acid added to this brown solution produces vigorous effervescence but no precipitate. It is probable that oxidation takes place here as with pyrogallol itself. This tendency of galleïn to oxidize is seen further in its action on silver nitrate, which it reduces to metallic silver.

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[1] Ann. Chem. (Liebig), **183**, 6.

[2] J. Phys. Chem., **2**, 173.

[3] Ann. Chem. (Liebig), **196**, 88.

[4] Cf. Collie and Tickle on "Salts of Dimethylpyrone and the Quadrivalence of Oxygen." J. Chem. Soc., **75**, 710.

Galleïn Tetracetate.

Galleïn tetracetate was made according to Buchka's directions—by boiling galleïn and an equal weight of sodium acetate in four times the weight of acetic anhydride for four hours. After a number of trials it was found that the acetylization was complete in one hour. The excess of acetic anhydride was distilled off and the residue poured into a large amount of water. The acetate appeared on the bottom of the vessel, partly in the form of crystalline particles, partly as an oil that soon solidified. The product thus obtained was filtered and when dry had a gray color; yield almost quantitative. Crystallized from benzene, it was obtained in colorless needles. Recrystallized from benzene, acetone, alcohol, and acetic acid in succession till no further change in its melting-point could be observed, it was found to melt at 241° C.[1] The melting-point as given by Buchka is 247° to 248°, by Herzig[2] 236° to 237°.

Crystals of galleïn tetracetate and gallin tetracetate, as well as of the so-called hydrogalleïn tetracetate, were examined by Professor A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows concerning them:

"Galleïn tetracetate crystallizes from a mixture of alcohol and chloroform in bright, transparent, triclinic crystals bounded by the faces c (001), b (010), m (110), M $(1\bar{1}0)$, and x $(10\bar{1})$. The corresponding angles vary considerably on different crystals, permitting only an approximate determination of the crystallographic constants: These are: a : b : c = 0.865 : 1 : 0.626.

$$\alpha = 74^\circ\ 2',\ \beta = 126^\circ\ 2',\ \text{and}\ \gamma = 99^\circ.$$

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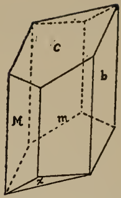
[1] All melting-points were determined by means of a thermometer compared with one standardized by the Physikalisch-Technische Reichsanstalt, Charlottenburg, Germany.

[2] Monatsh. Chem., **13**, 426.

"The more important anglesa re:

M : m = 72° 4′;
m : b = 54° 39′;
cm : = 69° 2′;
c : M = 52° 12′;
c : x = 99° 58′;
x : m = 47° 41′;
x : M = 64° 21′.



"On smaller crystals from ether it could be determined that the substance has a large optical angle, is positive, and has a strong dispersion, $v > \rho$. These crystals differ both in habitus and in angles from gallin tetracetate and the so-called hydrogalleïn tetracetate, leaving no doubt that they are a different substance.

"The crystals of gallin tetracetate and of the so-called hydrogalleïn tetracetate, while differing somewhat in habitus, show a similarity of angles in the principal zone, which is, in fact, identical within the limits of error arising from the imperfectness of the crystals. The mean angles were:

"Gallin tetracetate 79°.5, 42°, and 58°.5.

"Hydrogalleïn tetracetate 79°53′, 41°26′, and 58°41′.

Galleïn acetate is insoluble in a cold 5 per cent solution of sodium carbonate; the solution remains perfectly colorless, though allowed to stand two or three days. When boiled for some time there is partial saponification and a very small part of the acetate dissolves, as shown by the slight pink tinge of the carbonate solution.

When treated with a few drops of concentrated sulphuric acid in the cold, galleïn acetate dissolves, giving the acid solution a deep-red color. When diluted with water the solution retains its red color, and after standing some time deposits red crystals. These crystals, when filtered out and washed with a little water, dissolve in ammonium hydroxide with the purple color and in caustic potash solution with the deep-blue color so characteristic of galleïn, and give also the unmistakable test for galleïn with lead acetate. There can be no doubt that sulphuric acid saponifies the acetate, and the crystals that separate are those of galleïn.

The determination of the exact constitution of galleïn acetate was an urgent matter. The difficulty of deciding it by a combustion-analysis will be seen at once by a comparison of the percentages of carbon and hydrogen in galleïn acetate of different content of acetyl groups.

No. of CH_3CO groups.	C. Per cent.	H. Per cent.	Acetyl groups. Per cent.
4	63.16	3.78	32.34
5	62.72	3.86	37.46
6	62.34	3.92	41.89

From the above it will be seen that the percentage of carbon differs by about 0.4 per cent, hydrogen by about 0.07 per cent in the several cases. Buchka found $C = 63.52$ and 62.73, $H = 4.44$ and 3.82, results that agree as well with the assumption that this is a *pent*acetate as that it is a *tetr*acetate.

There is a much wider margin in the percentages of acetyl residues in the three supposed possible formulas, as shown in the last column in the above table. Four C_2H_3O groups would equal 32.34 per cent; five would equal 37.46 per cent, a difference of 5.12 per cent; six would equal 41.89 per cent of the whole molecule, a difference of 4.43 per cent.

Several attempts were made to determine the number of acetyl residues in the acetate by saponification by means of different alkalies, but without success, since the galleïn residue itself undergoes some decomposition when heated with alkalies, giving volatile acid products that have not been further investigated. It was found, however, that a modification of Wenzel's method[1] could be used satisfactorily. The distinguishing points of this method are: First, saponification by means of strong sulphuric acid; second, removal of free sulphuric acid by means of secondary sodium phosphate; third, distillation of the liberated acetic acid *in vacuo*. The three important modifications of the Wenzel method, suggested by this work, are: First, the substitution of distillation in steam for distillation *in vacuo*; second, the abandonment of one of the condensers; third, the use of dimethylamidoazobenzene as an indicator to detect and determine mineral acid in the distillate. The arrangement of the apparatus may be understood from the accompanying sketch: *A* is a 300 cc. distilling flask with delivery tube inclined upwards; *B* is a 100 cc. distilling flask with delivery tube inclined downwards so as to connect easily with *C*, an Allihn condenser. *D* is a 750 cc. Erlenmeyer flask, *F* a small separatory funnel, and *S* a screw-clamp.

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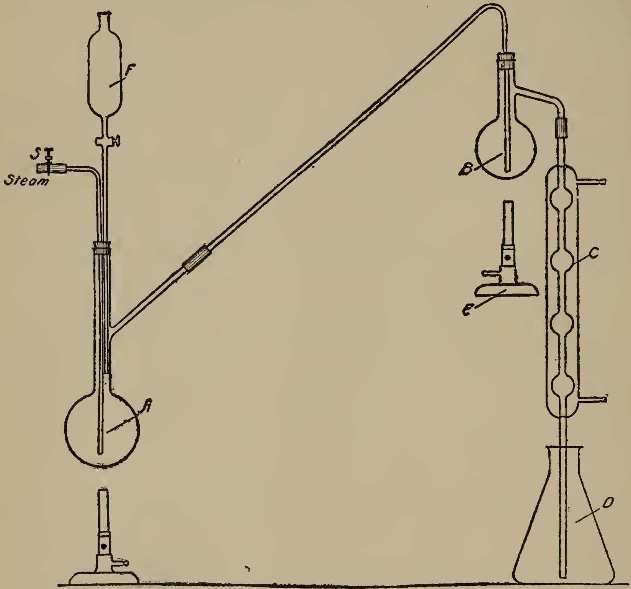
[1] Monatsh. Chem., 18, 659.



A weighed amount of material is placed in *A* and 3 or 4 cc. of sulphuric acid diluted with water (2 of acid with 1 of water by volume), run in through the funnel *F*, the screw-clamp *S* being closed. An excess of tenth-normal sodium hydroxide solution is measured into flask *D*, the whole apparatus properly connected, and water started through the condenser. The flask *A* is then heated for one hour to the temperature of a boiling water-bath, when 3 cc. of distilled water are added and the heat continued for half an hour longer. There are now introduced 20 cc. of a solution made by dissolving 45 grams of secondary sodium phosphate and 10 grams of glacial phosphoric acid in 100 cc. of water. Finally, add 50 cc. of boiled distilled water, heat with a burner, and pass in steam. Liquid will soon begin to collect in flask *B*, which serves as a trap to prevent acid from being carried over mechanically. When flask *B* is one-fourth full of liquid, heat it with a burner, the heat being so regulated as to keep the liquid at a constant level. When the distillate has collected in the receiver to the amount of 600 cc. stop the heat and transfer the distillate to a liter measuring-flask. Dilute to the mark and mix thoroughly. Measure out 500 cc. of the solution and titrate with tenth-normal hydrochloric acid, using phenolphthaleïn as an indicator. In order to tell whether any mineral acid (H_2SO_3, etc.,) has been carried over, the remaining portion is titrated with tenth-normal hydrochloric acid, using dimethylamidoazobenzene as the indicator. This is sensitive to free mineral acids but not to dilute organic acids. Of course, the amount of mineral acid is to be deducted from the total amount of acid found.

The process of distillation is not yet complete. One or two cc. of tenth-normal sodium hydroxide are again measured into flask *D*, and the heating continued until 300 cc. are collected. This is titrated directly with tenth-normal hydrochloric acid, using phenolphthaleïn as an indicator. The total amount of acid in this distillate is so small as to make the detection of mineral acid impossible—none was discovered in it in any determination made. To make sure that all volatile acid has been driven from flask *A*, a third distillate is collected which rarely showed more than 0.2 cc. tenth-normal sodium hydroxide neutralized. The net amount of tenth-normal sodium hydroxide neutralized, multiplied by 0.0043044 gives the weight of acetyl groups present. This method was used in all the acetyl determinations reported in this paper.

In order to test the apparatus and chemicals, preliminary determinations were made, using a compound of known composition—acetanilide. Two analyses of acetanilide were made by the method given above with the following results :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.5472	40.25	0.0	40.25	31.66
0.2260	16.85	0.0	16.85	32.09

Calculated percentage of C_2H_3O in acetanilide = 31.84.

Galleïn acetate analyzed according to this method gave the following results :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid.	Net tenth-normal sodium hydroxide . cc.	C_2H_3O . Per cent.
0.1946	15.1	0.3	14.8	32.74
0.2584	19.7	0.0	19.7	32.82

Calculated[1] for $C_{20}H_7O_7(C_2H_3O)_5$, 37.46 per cent C_2H_3O.
Calculated for $C_{20}H_8O_7(C_2H_3O)_4$, 32.34 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_3$, 26.33 per cent C_2H_3O.

There can be no doubt from these results that this is a tetracetate of galleïn.

GALLEÏN TETRABENZOATE.

Buchka made this compound by use of benzoyl chloride. It was deemed advisable to try making it from benzoic anhydride. Galleïn (10 grams) and benzoic anhydride (50 grams) were heated to 190° C. on a metal-bath for seven hours. The melt was then transferred to a 2-liter round-bottomed flask and the excess of benzoic anhydride removed with steam. The black residue was filtered out and, after draining thoroughly, dissolved in acetone and boiled with boneblack. The acetone solution was concentrated and a little water added. In a short time yellow crystals appeared which, by repeated crystallization from acetone, alcohol, and acetic acid, became white and melted at 226°. Melting-point given by Buchka is 231°.

Efforts were made to determine the number of benzoyl residues in this compound by the method used in analyzing the acetate, but failed on account of the difficulty of completely saponifying the benzoate by sulphuric acid. But that it contains four benzoyl groups can scarcely be doubted from its analogy to the tetracetate.

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[1] In all calculations in this paper the following atomic weights have been used: O = 16, H = 1.008, C = 12.01, N = 14.04, Ag = 107.92, I = 126.85, S = 32.07, Pb = 206.92.

HYDROGALLEÏN TETRACETATE.

The preparation of this compound from the so-called hydrogalleïn, and its identity with galleïn tetracetate, constitute the basis for Buchka's formula for galleïn. It will be remembered, however, that Herzig tried to make it from Buchka's hydrogalleïn, but did not succeed.

Pure galleïn (made by saponifying the acetate melting at 241°) was dissolved in slight excess of potassium hydroxide solution, zinc dust added cautiously, and the temperature of the contents of the flask prevented from rising by a stream of cold water around the flask. When the blue color of the alkaline solution disappeared, becoming more or less brown, dilute sulphuric acid was added slowly and in such a way as to prevent an appreciable rise in temperature. The acid liquid was extracted with ether, the ether solution rapidly filtered to remove suspended particles, and dried over calcium chloride in an atmosphere of carbon dioxide. The ether solution was then distilled in a stream of carbon dioxide. An oil with a slight red color remained and on standing solidified. Acetic anhydride in excess was added and the liquid boiled on a metal-bath, for four hours, in a flask connected with a reflux condenser. A portion of the excess of acetic anhydride was distilled off and the residue poured into water. The acetate collected on the bottom of the vessel as an oil, which afterwards solidified. The yellow substance was crystallized from benzene, and gave a product melting at 213°–214°. It was recrystallized from alcohol and acetic acid in succession till the melting-point was constant. The final product was colorless and melted at 216°.

These crystals were examined by Dr. Gill, of the Mineralogical Department of the University, and compared with crystals of gallin tetracetate. The crystals of both were found to be triclinic and the angle measurements in the principal zones were the same within the limits of error. In all probability, therefore, the hydrogalleïn and gallin tetracetates are crystallographically identical.

The difference between hydrogalleïn and galleïn acetate is seen in their conduct with sodium carbonate and concentrated sulphuric acid. The former, when treated with a five per cent solution of sodium carbonate in the cold, dissolves at once, imparting to the solution at first a greenish-yellow fluorescence; the color rapidly deepens, becoming later a decided purple, owing to saponification and oxidation. The hydrogalleïn acetate, when treated with a few drops of cold concentrated sulphuric acid, dissolves with a red color. When this solution is diluted with water it forms a green solution which, after standing, deposits a green precipitate. This, filtered off and washed with a little water, dissolves in ammonium hydroxide with the green color and in aniline with the blue color, both characteristic of coeruleïn. Sulphuric acid saponifies the so-called hydrogalleïn acetate and condenses one of the products (gallin) even in the cold to coerulin, which is easily oxidized in alkaline solution to coeruleïn, forming a green solution with ammonium hydroxide, and dissolving in aniline with a blue color.

Analyses for the purpose of determining the number of acetyl groups in this compound gave the following results:

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2328	21.5	4.0	17.5	32.36
0.1690	15.7	2.75	12.95	32.98

Calculated for $C_{20}H_{11}O_7(C_2H_3O)_3$, 26.22 per cent C_2H_3O.
Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_5$, 37.33 per cent C_2H_3O.

Clearly the compound is a tetracetate, but it has none of the characteristics of galleïn tetracetate but all the properties of gallin tetracetate described below.

We repeated this experiment a great number of times, following Buchka's directions to the letter but always with the same result. The product was absolutely identical in every respect with gallin tetracetate. We must hence conclude that hydrogalleïn and its acetate do not exist.

GALLIN TETRACETATE.

This compound was made by the method given by Buchka. Galleïn, dissolved in ammonium hydroxide, was reduced to gallin by means of zinc dust, the solution being kept at the boiling-point. After boiling thus for two hours, the purple color having disappeared, dilute sulphuric acid was added little by little through the condenser-tube till in slight excess. The acid solution was filtered while hot and cooled in an atmosphere of carbon dioxide. It was then shaken with ether to dissolve the gallin, the ether solution separated and filtered, dried over calcium chloride in an atmosphere of carbon dioxide, and finally the ether distilled off in a current of carbon dioxide. The residue, gallin, appeared as a red oil which solidified on standing. This was converted into the acetate in accordance with the directions given under hydrogalleïn tetracetate. The crude material was recrystallized from alcohol and acetic acid and gave a colorless product melting at 216° C. Its conduct with a five per cent solution of sodium carbonate and with concentrated sulphuric acid was identical with that of the so-called hydrogalleïn acetate described above.

The difficulty of deciding the composition of gallin acetate by combustion-analysis will appear from the following table, which gives the percentages of carbon and hydrogen according to the different formulas:

No. of acetyl groups.	C. Per cent.	H. Per cent.
3	63.41	4.09
4	62.92	4.15
5	62.50	4.20

Buchka found C = 62.72 per cent; H = 4.37 per cent.

Determinations of the number of acetyl groups in gallin acetate resulted as follows:

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O Per cent.
0.2490	20.3	1.5	18.8	32.50
0.1728	14.4	1.2	13.2	32.88

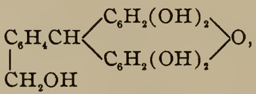
Calculated for $C_{20}H_{11}O_7(C_2H_3O)_3$, 26.22 per cent C_2H_3O.
Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.
Calculated for $C_{20}H_9O_7(C_2H_3O)_5$, 37.33 per cent C_2H_3O.

In view of these results this compound is correctly called gallin tetracetate.

The residue in flask *A* (see sketch), when treated with an excess of caustic potash, gives a blue color, as would be expected of gallin in presence of air.

GALLOL ACETATE.

Buchka claims to have obtained a lower reduction-product of galleïn by the use of zinc dust and acid solution. Having the formula as given by him,



$$\begin{array}{l} C_6H_4CH\left\langle\begin{array}{l}C_6H_2(OH)_2\\ C_6H_2(OH)_2\end{array}\right\rangle O, \\ | \\ CH_2OH \end{array}$$

gallol would be expected to yield a pentacetate. According to Buchka's method for making this substance, galleïn (5 grams) was placed in a liter flask with 700 cc. of water, a little dilute sulphuric acid added, and some zinc dust. The solution was kept boiling for ten hours, small amounts of dilute acid and zinc dust being added from time to time. The solution lost its deep-red color and became straw-yellow. It was then filtered and allowed to cool. A small deposit of crystals appeared after awhile on the bottom of the vessel. The solution was shaken with ether and the ether dried and distilled off with the same precautions as noted under hydrogalleïn tetracetate. A residue was left as a red oil, to which were added the crystals which had separated, and the whole acetylized. The acetate was recrystallized from alcohol, yielding colorless crystals melting sharply at 216°. Buchka's gallol pentacetate melted at 230°.

The product made as above described reacted with a 5 per cent solution of sodium carbonate and with concentrated sulphuric acid in every respect as the gallin tetracetate and could not be distinguished from it in any way. A determination of the number of acetyl groups resulted thus :

Weight of substance. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2237	20.5	3.46	17.04	32.79

Calculated for $C_{20}H_{10}O_7(C_2H_3O)_4$, 32.21 per cent C_2H_3O.

A pentacetate, according to Buchka's formula, would have 38.26 per cent C_2H_3O. This substance, therefore, not only shows all the characteristics of gallin tetracetate but the results obtained on analysis prove the identity of the two products.

An attempt was made to reduce galleïn in acetic acid solution to gallol by the action of sodium amalgam, with negative results. Only gallin tetracetate could be isolated.

An effort was made to prepare gallol acetate directly from galleïn acetate. Galleïn (5 grams) was mixed with an equal weight of sodium acetate and 25 grams acetic anhydride and boiled in a flask connected with a return-condenser for one hour. Zinc dust in small amounts was added from time to time, while the boiling was continued for three hours. A small quantity of the material was taken out, the acetate formed crystallized once from alcohol and found to melt at 215°, and to dissolve in dilute ammonia with a purple color. The remainder of the mixture was boiled seven hours longer, zinc dust in small quantities being added from time to time. The product crystallized once from alcohol, melted at 214°.5, and dissolved in dilute ammonia with a purple color. Thus it would appear to be impossible to obtain gallol by reduction of galleïn or its acetate with zinc dust in acid solution, even on prolonged heating.

METHOD FOR THE PREPARATION OF GALLIN TETRACETATE.

As a result of this work, however, a method for the preparation of gallin acetate was found which is very much shorter and simpler than that described by Buchka, and gives a yield almost as great as that required by theory. To 5 grams of galleïn add 5 grams of fused sodium acetate and 20 cc. of acetic anhydride. Boil in a flask connected with a return-condenser for fifteen minutes, add 2 grams zinc dust, and boil fifteen minutes longer. Allow the excess of zinc dust to settle to the bottom of the flask and pour off the solution carefully into a half liter of water. A small portion of the precipitate is granular; the bulk of it is an oil which soon solidifies, especially when agitated. Recrystallize from acetic acid (40 per cent), using boneblack to decolorize, afterwards from alcohol slightly diluted with water.

SILVER SALT OF GALLIN TETRACETATE.

That gallin tetracetate is an acid was shown not only by its dissolving in dilute sodium carbonate solution but also by making its silver salt. Gallin acetate was dissolved in 95 per cent alcohol and an alcoholic solution of silver nitrate added in excess. The mixture was heated to boiling, filtered, and left in the dark for several hours. There separated a white precipitate resembling, in appearance, silver chloride. It was practically insoluble in alcohol when once precipitated, did not melt sharply, but decomposed when heated, and turned dark when exposed to sunlight.

The so-called gallol acetate gave rise to the same compound under the same conditions—another proof of the identity of gallin and gallol acetates.

On analysis the compound gave the following results for silver.

	Weight of substance. Gram.	Weight of silver. Gram.	Silver. Per cent.
I	0.1044	0.0172	16.48
II	0.1072	0.0179	16.70

Calculated for $C_{20}H_9O_7(CH_3CO)_4Ag$, 16.83 per cent Ag.

The analysis was made by placing the well-washed and dried product in a small porcelain crucible and burning out the organic matter by careful ignition.

The first analysis above was made from a product obtained from the so-called gallol acetate, the second from gallin acetate.

GALLEÏN METHYL ESTER.

This compound was made by one of the usual methods for the preparation of esters. Galleïn (5 grams), methyl alcohol

(30 cc.), and concentrated sulphuric acid (10 cc.) were mixed, forming a deep-red solution. This was boiled in a flask connected with a return-condenser for one and one-quarter hours, when there separated a good quantity of crystals. The mass was then poured into 500 cc. water, filtered, the residue washed and dried, at first in the air, finally in an air-bath at 70°. To free the ester from any galleïn which might have been present, the ester was dissolved in ether, in which galleïn is insoluble, the solution filtered and concentrated. The ester came down in granular masses of dark red color, with bronzy luster. It dissolves in alcohol, acetone, ether, chloroform, acetic ether with red color, but is almost insoluble in benzene. It dissolves at once in alkalies and alkaline carbonates with the colors characteristic of free galleïn in these solvents—probably owing to saponification. It did not melt when heated to 280° C.

A determination of the methoxy group by Zeisel's method in a sample dried at 100° C. resulted as follows:

Weight of ester. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1819	0.1011	7.34

Calculated for $C_{19}H_8O_2(OH)_3COOCH_3$, 8.20 per cent.

GALLEÏN ETHYL ESTER.

Galleïn (5 grams), absolute alcohol (30 cc.), and concentrated sulphuric acid (20 cc.) were heated in a flask provided with a return-condenser for two and three-quarters hours. The galleïn was entirely in solution at the beginning of the operation and, while still heating, crystals in good quantity were deposited. The mixture was poured into 500 cc. water, filtered, and washed. The ester appeared as beautiful crystals, red by transmitted light, green by reflected light. It dissolves in alcohol, acetone, ether, chloroform, and acetic ether with red color. Quite a number of efforts were made to crystallize it from different solvents, but the best method of purifying it was found to be solution in anhydrous ether, filtering to remove galleïn, and concentration of the solution almost to dryness. The ester then appeared as granular masses.

Analysis of a sample dried at 100° C. to constant weight gave, by Zeisel's method, the following result :

Weight of ester. Gram.	Weight of silver iodide. Gram.	C_2H_6O. Per cent.
0.0811	0.0518	12.25

Calculated for $C_{19}H_8O_2(OH)_3COOC_2H_5$, 11.48 per cent.

The results obtained with the methyl and the ethyl esters of galleïn indicate very clearly that galleïn is an acid and contains one carboxyl group. It is probable that what Baeyer considered alcohol of crystallization was in reality due to the presence of this ester.

GALLEÏN TRIPHENYLCARBAMATE.

By the action of phenyl isocyanate upon galleïn, combination took place, giving rise to a new compound. Galleïn dried at 100° C., and a little more than the calculated amount of phenyl isocyanate, were heated quickly to the boiling-point of the mixture and kept at this temperature for ten minutes—agitating from time to time. On cooling, the residue appeared as a black tar. This was taken up in benzene, the solution filtered, boiled with boneblack, and allowed to stand. A small amount of a crystalline deposit appeared which was filtered out and found to consist largely of diphenyl urea. To the filtrate petroleum ether was added, when there appeared a bulky yellow precipitate. This was filtered out and dissolved in a little chloroform. On standing, some white crystals appeared which did not saponify with caustic potash solution, and melted at 235° C., and were probably diphenyl urea. This was removed by filtration and the galleïn phenylcarbamate precipitated from the chloroform solution by petroleum ether, filtered out, and the process of dissolving in chloroform and precipitating with petroleum ether continued till no further signs of diphenyl urea appeared.

The galleïn carbamate thus made is a solid, with a light yellow color. It does not melt sharply on account of decomposition and dissolves in alcohol and acetone with green fluorescence. It is an acid, as is shown by the fact that it is soluble in cold dilute sodium carbonate solution with purple color, which is changed to red by acids. The red color of the acid solution is not changed to purple by ammonia solution as would be the case were galleïn formed here. The carbamate dissolves also in a cold dilute solution of ammonia with color, green by reflected light, red by transmitted light. In caustic alkali it dissolves (apparently with saponification) giving a deep-blue solution.

The nitrogen in this compound was determined by Dafert's modification of the Kjeldahl method. A weighed amount of carbamate was placed in a 300 cc. digesting flask, 10 cc. of alcohol added to dissolve it, 30 cc. dilute sulphuric acid (1 : 5) added, and a small amount of zinc dust. The mixture was heated in a flask fitted with a return-condenser till the color nearly disappeared. The flask was then disconnected from the condenser, and the alcohol and water evaporated till the organic matter first showed signs of charring. The remainder of the process was that of the Gunning modification of the ordinary Kjeldahl method. The following results were obtained :

	Weight of carbamate.	Tenth-normal ammonia.	Amount of nitrogen.	
	Gram.	cc.	Gram.	Per cent.
1	0.4274	18.0	0.025272	5.91
2	0.2711	11.4	0.0160056	5.90
3	0.1966	7.8	0.0109512	5.57
4	0.2116	8.3	0.0116532	5.51
5	0.2204	8.7	0.0122148	5.54
6	0.2372	9.35	0.0131274	5.53

Calculated for $C_{20}H_9O_7(OCNHC_6H_5)_3$, 5.83 per cent N.

Calculated for $C_{20}H_8O_7(OCNHC_6H_5)_4$, 6.68 per cent N.

Calculated for $C_{20}H_8O_7(OCNHC_6H_5)_2$, 4.67 per cent N (the formula for this compound on the basis of Buchka's formula for galleïn).

The analyses above recorded were made from two samples which were prepared at different times—1 and 2 from one, 3, 4, 5, and 6 from the other. The results can lead to but one conclusion, that there are three phenyl isocyanate residues introduced and that the compound is galleïn triphenylcarbamate.

GALLEÏN BASIC LEAD SALT.

A sodium carbonate solution was boiled with an excess of galleïn till there was no further evolution of gas. This solution was then filtered from the excess of galleïn and an excess of lead acetate solution added. The precipitate was filtered out and washed till the wash-water no longer gave a test for lead, and dried at 120° C. The lead compound was a dark-blue powder. On analysis for lead the following results were found :

Weight of substance. Gram.	Weight of Lead sulphate. Gram.	Lead. Per cent.
0.9343	0.8960	65.49
0.1975	0.1880	65.0

Calculated for $C_{20}H_8O_7(PbOH)_4$, 65.90 per cent Pb.

GALLEÏN TRIMETHYL ETHER.

Five grams of galleïn were dissolved in 200 cc. of methyl alcohol, 4 grams of caustic potash in 50 cc. methyl alcohol, the two solutions united, and a portion (100 cc.) of the solvent distilled off. To the residue was added methyl iodide (15 grams), and the whole heated to boiling on a water-bath for twenty to thirty hours. At intervals of about eight hours, 1 or 2 grams of solid caustic potash were added, heated for one hour, and about 5 grams methyl iodide added. The solution, at first blue, quickly becomes red. After sufficient heating, the methyl alcohol and excess of methyl iodide were distilled off on a water-bath, the residue treated with 500 cc. of a one per cent solution of potassium hydroxide to dissolve any partially methylated products, and filtered. The insoluble residue will be considered in connection with the tetramethyl ethers.

The alkaline filtrate was acidified with a little concentrated hydrochloric acid. A yellow precipitate was thrown down which was filtered out and washed. The dried residue was dissolved in acetone, boiled with boneblack, concentrated, a little water added, and allowed to stand. After a few hours there was a good yield of crystals which had a golden-yellow color. These were then dissolved in alcohol, boiled with boneblack, concentrated, and allowed to crystallize—a little water being added. Additional crops of crystals were obtained by further dilution of the mother-liquors. By repetition of this treatment crystals were finally obtained which were colorless and melted at 229°.

Determinations of the number of methoxy groups present were made by Zeisel's method. Apparatus and chemicals were first tested by making a determination of the methoxy group in anisic acid, with the following result:

Weight of anisic acid. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1905	0.2910	20.19

Calculated for $C_6H_4(OCH_3)COOH$, 20.39 per cent CH_3O.

The following results were obtained with the galleïn methyl ether dried at 100° C.:

Weight of ether. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1866	0.3100	21.96
0.2376	0.3966	22.06

Calculated for $C_{20}H_8O_5(OCH_3)_2$ according to Buchka's formula),[1] 15.90 per cent CH_3O.

Calculated for $C_{20}H_9O_4(OCH_3)_3$, 22.91 per cent CH_3O.

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.

The substance is hence a trimethyl ether.

The best method for making the galleïn trimethyl ether in excess is as follows: The galleïn (1 molecule) is dissolved in methyl alcohol in the proportions given above, the calculated amount of caustic potash (4 molecules), also dissolved in methyl alcohol, is added, and from one-third to one-half of the alcohol is distilled off on the water-bath. An excess of methyl iodide is then added, the flask connected with a reflux-condenser, and the mixture is kept gently boiling on the water-bath for ten hours. The alcohol and excess of methyl iodide are then distilled off on the water-bath, and the dry residue treated with a one per cent solution of caustic potash. The rest of the treatment is as given above. Repeated additions of caustic potash and methyl iodide and longer heating increase the yield of the galleïn tetramethyl ether.

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[1] The solubility of this ether in alkaline solutions is a further argument against the correctness of Buchka's formula for galleïn.

Some of the galleïn trimethyl ether recrystallized from ether was examined by Dr. Gill. The crystals were found to be triclinic. The dispersion was strong, $v > \rho$. The optical angle was large and the crystals were optically positive.

Galleïn trimethyl ether dissolves in alcohol and acetone with a delicate pink tint; in benzene its solution is colorless. It resembles phenolphthaleïn quite closely. In dilute sodium carbonate solution, in dilute ammonia, as well as in caustic alkalies, it dissolves at once, even in the cold, with a deep-red color. From such solutions, by the addition of acids, it is precipitated again as the colorless trimethyl ether.

This galleïn trimethyl ether was also made by saponification of the colored tetramethyl ether as stated below.

TRIMETHYL GALLEÏN MONACETATE.

Galleïn trimethyl ether was mixed with an equal weight of fused sodium acetate and five times its weight of acetic anhydride, and the mixture kept at the boiling-point for one hour. The excess of acetic anhydride was distilled off and the residue poured into a large bulk of water. The precipitate was at first oily, but soon solidified. This was filtered off and washed. The residue thus obtained was recrystallized from alcohol. The crystals were needle-shaped and colorless, showed double refraction, and were either monoclinic or triclinic. Melting-point 197°. They dissolve in alcohol, acetone and chloroform, are insoluble in cold aqueous caustic potash, but after prolonged boiling they dissolve, giving a red color to the solution (apparently after saponification of the acetyl group). Saponification takes place more readily in alcoholic caustic potash.

The product dried at 100° C. and analyzed for methoxy groups gave the following results :

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.2004	0.3028	19.97
0.1690	0.2570	20.10

Calculated for $C_{20}H_8O_4(OCH_3)_3(C_2H_3O)$, 20.76 per cent CH_3O.

The results of these analyses show that this derivative of galleïn contains three methoxy groups and one acetyl group. Its properties also harmonize with this view.

GALLEÏN TETRAMETHYL ETHER—COLORED.

The residue insoluble in alkalies, obtained in making the trimethyl ether of galleïn, was dissolved in 50 per cent alcohol, boiled with a little boneblack to remove gummy material, concentrated, and allowed to crystallize. Two distinct sets of crystals were deposited. One set consisted of pyramidal crystals belonging to the monoclinic system. They were red, the larger ones exhibiting a bronzy luster. By far the larger proportion of the crystals was of this sort. The others were much lighter in color and were needle-shaped. These latter will be discussed under the head of galleïn tetramethyl ether—colorless.

The dark-red crystals, mentioned above, melt sharply at 199°, dissolve in alcohol, acetone, chloroform, ether, and acetic ether, with red color. The ether is insoluble in cold alkalies; in hot alkalies it forms a red solution—after saponification. To an alcoholic solution of the ether a solution of sodium carbonate was added, the solution evaporated to dryness on a steam-bath, the residue dissolved in water and filtered, the filtrate acidified, when there appeared a precipitate with a yellow color. This was filtered out, recrystallized from alcohol, and found to be colorless and to melt at 229°. The product showed also all the other characteristics of the galleïn trimethyl ether already described. The number of methoxy groups in the colored methyl ether was determined with the following results :

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1770	0.3828	28.59
0.2140	0.4656	28.76

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.
Calculated for $C_{20}H_9O_4(OCH_3)_3$, 22.91 per cent CH_3O.

This ether is unquestionably a galleïn tetramethyl ether, and since one of the methyl groups may be split off by the action of sodium carbonate solution, leaving a product with three methyl groups (see galleïn trimethyl ether above), one of the methyl groups must replace a hydrogen atom of a carboxyl group; *i. e.*, the substance is a monomethyl ester of trimethyl galleïn.

GALLEÏN TETRAMETHYL ETHER—COLORLESS.

The light-colored, needle-shaped crystals referred to above were separated from the deep-red ones, dissolved in acetic acid, boiled with boneblack, and filtered. The slightly red solution was diluted with water till a precipitate appeared, then heated till all dissolved, and allowed to cool slowly. The crystals which separated still had some color. To remove this they were dissolved in alcohol, a little potassium hydroxide was added, and the solution heated to boiling. This saponified the colored ether, forming the potassium salt of the trimethyl ether, which is easily soluble in water. The alcoholic solution diluted with water yields colorless crystals of the tetramethyl ether. These are needle-shaped, show double refraction, and are either monoclinic or triclinic.

The same compound was obtained by heating galleïn trimethyl ether with an excess of methyl iodide in a sealed tube to 125° C. for five hours.

The colorless ether melts at 195°, is soluble in alcohol, acetone, and chloroform, but to a less degree than the colored ether. It is insoluble in aqueous caustic potash (laboratory reagent) even on boiling.

Analysis of a sample dried at 100° C. gave the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.0804	0.1751	28.77

Calculated for $C_{20}H_8O_3(OCH_3)_4$, 29.53 per cent CH_3O.

GALLEÏN TETRAETHYL ETHER—COLORED.

Galleïn (5 grams) was dissolved in 200 cc. of methyl alcohol,[1] caustic potash (4 grams) in 50 cc. of the same solvent and the two united. A portion (100 cc.) of the solvent was distilled off, and to the residue was added an excess of ethyl iodide. The color changes from blue to red. The mixture was kept at the boiling-point for from five to ten hours. The methyl alcohol and the excess of ethyl iodide were then distilled off on a water-bath. The residue was treated with 500 cc. of a one per cent solution of potassium hydroxide to dissolve any partially ethylated products, and filtered. From the filtrate was separated the triethyl ether as described below.

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[1] Methyl alcohol was used in this case because it is a better solvent than ethyl alcohol for the potassium salt of galleïn.

The residue insoluble in alkali was a deep red viscous mass, which slowly hardened. This was dissolved in methyl alcohol, boiled two or three times with boneblack to remove gummy impurities, concentrated, and allowed to stand several days. There appeared first needle-shaped crystals, which were filtered out and are described below as the colorless tetraethyl ether. After these, in greater amount, came tabular, monoclinic crystals of a deep-red color, which melted at 155°, and whose corresponding angles were the same as those of the colored tetramethyl ether. This ether dissolves in methyl alcohol, ethyl alcohol, acetone, chloroform, acetic ether, and acetic acid. In cold alkalies it is insoluble. If some of the ether is dissolved in alcohol, a little sodium carbonate or potassium hydroxide added, and the mixture heated to dryness on a water-bath, it undergoes saponification. This was shown by dissolving the residue in water, filtering, acidifying the filtrate, when a yellow precipitate was thrown down. This product, on recrystallization, proved to be colorless, and showed the characteristic properties of the triethyl ether described below.

The following are the results of determinations of the ethoxy groups:

Weight of substance. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.2015	0.3788	36.08
0.1199	0.2356	37.71

Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.
Calculated for $C_{20}H_9O_4(OC_2H_5)_3$, 30.14 per cent C_2H_5O.

From the above analyses, as well as from the method of its preparation and its properties and reactions, this ether is the analogue of the colored galleïn tetramethyl ether.

GALLEÏN TETRAETHYL ETHER—COLORLESS.

The needle-shaped crystals referred to in connection with the colored tetraethyl ether after recrystallization from alcohol, using boneblack to decolorize, were obtained almost colorless, and found to melt at 144°. They dissolve in alcohol, acetone, acetic acid, and chloroform, but less easily than the colored variety. This ether is insoluble in aqueous alkalies, even on boiling. Analysis gave the following result for the ethoxy group :

Weight of ether. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.0682	0.1301	36.61

Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.

GALLEÏN TRIETHYL ETHER.

The alkaline filtrate obtained in the preparation of galleïn tetraethyl ether was acidified with concentrated hydrochloric acid. A heavy yellow precipitate was thrown down. This was filtered out, washed well, and recrystallized from alcohol, using boneblack to decolorize. Colorless crystals were obtained which, on analysis, gave the following result:

Weight of substance. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.1057	0.1765	32.04

Calculated for $C_{20}H_9O_4(OC_2H_5)_3$, 30.14 per cent C_2H_5O.
Calculated for $C_{20}H_8O_3(OC_2H_5)_4$, 37.82 per cent C_2H_5O.

Galleïn triethyl ether dissolves easily in most of the organic solvents. In cold dilute sodium carbonate solution, in dilute ammonia, as well as in the caustic alkalies, it dissolves at once with deep-red color, just as phenolphthaleïn does. On acidifying these solutions the colorless triethyl ether is reprecipitated.

GALLIN PENTAMETHYL ETHER.

Galleïn was reduced by zinc dust in alkaline solution, and, after acidifying, the resulting gallin extracted with ether in the usual way. After complete removal of the ether by distillation in carbon dioxide, the flask containing the residue was connected with a return-condenser and also a hydrogen generator. After removing as completely as possible all air from the apparatus by means of hydrogen, a slight excess of potassium hydroxide dissolved in 95 per cent alcohol was added through the condenser-tube. The solution turned light-blue due to slight oxidation. After heating five minutes an excess of methyl iodide was added and the mixture heated to boiling on a water-bath for ten hours. The alcohol and excess of methyl iodide were distilled off and the residue treated with 500 cc. of a one per cent solution of caustic potash. The residue was filtered out, washed, and recrystallized from alcohol, using boneblack to decolorize. The crystals at first were more or less yellow; recrystallized from alcohol and acetic acid in succession they became almost white and melted at 127°.

Analyses gave the following results:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1596	0.4167	34.51
0.1877	0.4887	34.42

Calculated for $C_{20}H_9O_2(OCH_3)_5$, 35.55 per cent CH_3O.
Calculated for $C_{20}H_{10}O_3(OCH_3)_4$, 29.38 per cent CH_3O.

The compound is therefore the pentamethyl ether of gallin.

The ether dissolves readily in alcohol, acetone, and acetic acid. It is insoluble in cold alkalies, but may be saponified by the method already outlined in connection with the colored galleïn tetralkyl ethers, giving a product that is colorless and dissolves in alkalies without color.

II. COERULEÏN.

The coeruleïn used for the following investigation was also furnished by the Badische Anilin und Soda Fabrik, and was of exceptional purity.

It was found that if coeruleïn is pulverized and suspended in water, it can be dissolved by saturating the water with sulphur dioxide. This filtered solution, when boiled for some time to remove the gas, was decomposed and coeruleïn precipitated. When filtered out and dried, it had a beautiful bronzy luster and seemed to be crystallized.

One marked difference between galleïn and coeruleïn is that while the former dissolves easily in a solution of sodium carbonate the latter is practically insoluble in such a solution, imparting to it only a faint yellow color even after boiling for some time.

In aniline, pyridine, and quinoline, coeruleïn dissolves, more readily if heated. In aniline it forms a deep-blue solution, the color remaining unchanged in excess of acetic acid. The solution in pyridine is colored greenish-blue, which turns purple in excess of acetic acid. On boiling with quinoline the color is purple, which becomes greenish-blue on cooling, and green when diluted with more quinoline.

COERULEÏN TRIACETATE.

Coeruleïn acetate was made according to the method given by Buchka—by boiling coeruleïn with sodium acetate and excess of acetic anhydride. After completion of the reaction a part of the acetic anhydride was distilled off and the residue poured into water. The red precipitate was filtered out and washed. Unsuccessful attempts were made to crystallize the acetate from glacial acetic acid, alcohol, acetone, chloroform, benzene, and acetic ether, in each of which it dissolves with red color. It was finally purified by dissolving it in acetone, filtering, evaporating to small bulk, and precipitating the acetate by adding to the acetone solution a saturated solution of sodium chloride. After washing till the filtrate gave no reaction for chlorides and drying, coeruleïn acetate appeared as a reddish-brown powder.

That it is coeruleïn triacetate cannot be doubted from the following determinations of the number of acetyl groups present :

Weight of acetate. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.2153	16.79	2.55	14.24	28.47
0.1753	13.50	2.05	11.45	28.12

Calculated for $C_{20}H_7O_6(C_2H_3O)_3$, 27.33 per cent C_2H_3O.
Calculated for $C_{20}H_6O_6(C_2H_3O)_4$, 33.47 per cent C_2H_3O.

The difficulty of deciding by combustion analysis how many acetyl groups this compound contains will be seen from the following table:

No. of acetyl groups.	Per cent C.	Per cent H.
3	66.10	3.41
4	65.37	3.53

Buchka found C = 65.7 and 66.71, and H = 3.75, but nevertheless calls the compound the triacetate.

COERULIN PENTACETATE.

Buchka's directions were followed in the preparation of this compound, using 5 grams of coeruleïn, 25 grams of acetic anhydride, and a little zinc dust. After heating for twenty minutes the mass began to solidify and had a dark-green color. The contents of the flask were transferred to a porcelain evaporator and heated on the water-bath till nearly all the acetic anhydride disappeared. The residue was then put into 1200 cc. of water to remove all zinc salts, etc., filtered, and washed. The mass was dark-green. Recrystallized from glacial acetic acid, the acetate appears in greenish-yellow needles, which show parallel extinction and form a felted mass. Solutions of coerulin acetate in acetic acid, alcohol, acetone, and chloroform have a greenish-yellow fluorescence. Buchka gives the melting-point of this compound as 256° C. This could not be verified—the compound decomposed when heated and did not melt at all.

Determinations of the number of acetyl groups in this compound resulted as follows:

Weight of acetate. Gram.	Tenth-normal sodium hydroxide. cc.	Mineral acid. cc.	Net tenth-normal sodium hydroxide. cc.	C_2H_3O. Per cent.
0.1837	19.9	3.05	16.85	39.48
0.1991	20.55	2.25	18.3	39.56

Calculated for $C_{20}H_8O_6(C_2H_3O)_4$, 33.34 per cent C_2H_3O.
Calculated for $C_{20}H_7O_6(C_2H_3O)_5$, 38.54 per cent C_2H_3O.
The product is therefore a pentacetate.

Calculated percentages of carbon and hydrogen are as follows:

No. of C_2H_3O groups.	Per cent C.	Per cent H.
4	65.11	3.90
5	64.51	3.97

Buchka found C = 65.31 and 64.64, H = 4.60 per cent, and on the basis of these analyses pronounced the compound a tetracetate. In the number of acetyl groups present, however, there is a much greater difference in the percentages for four and for five groups, and according to the results of the analyses given above it cannot be doubted that the compound is in reality coerulin pentacetate.

COERULEÏN MONOMETHYL ETHERS.

Coeruleïn (7 grams) and potassium hydroxide (3.5 grams) were dissolved in 150 cc. methyl alcohol and digested for one hour at the boiling-point of the mixture. There was then added an excess of methyl iodide and the whole boiled on a water-bath for twenty hours, adding at intervals of eight hours 2 grams of potassium hydroxide and boiling to make sure of solution, then slight excess of methyl iodide. The excess of methyl iodide and the methyl alcohol were then removed by distillation on a water-bath, the residue treated with 500 cc. of a one per cent solution of potassium hydroxide, and filtered. The insoluble residue will be described below.

The alkaline filtrate was acidified and a heavy dark precipitate was thrown down and filtered out. The precipitate was dissolved in boiling alcohol, filtered, and on standing there were deposited crystals of a dark color, with bronzy luster. The compound decomposes when heated and does not melt. It dissolves in alcohol, acetone, pyridine, aniline, and potassium hydroxide solution, imparting an olive-brown color to the solution in each case.

A determination of methoxy groups gave the following result:

Weight of ether. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.2365	0.1703	9.52

Calculated for $C_{20}H_9O_5(OCH_3)$, 8.61 per cent CH_3O.
Calculated for $C_{20}H_8O_4(OCH_3)_2$, 16.58 per cent CH_3O.

The compound is therefore coeruleïn monomethyl ether.

The mother-liquor from which this ether was obtained was allowed to evaporate spontaneously, when another crop of crystals appeared. This compound, when dried and analyzed for methoxy groups, gave the following result:

Weight of substance. Gram.	Weight of silver iodide. Gram.	CH_3O. Per cent.
0.1216	0.0755	8.21

Calculated for $C_{20}H_9O_5(OCH_3)$, 8.61 per cent CH_3O.

It is clearly a coeruleïn monomethyl ether but has different properties from those of the coeruleïn ether described above. It dissolves in acetone and pyridine with a purple color, in alcohol and aniline with a greenish-blue color, in potassium hydroxide solution with a light-green color. It is uniformly more soluble than the isomeric compound already described.

COERULEÏN METHYL ETHER—INSOLUBLE IN ALKALI.

The residue insoluble in alkali (see above under coeruleïn monomethyl ether) was dissolved in alcohol, the solution filtered and concentrated. After standing, a tarry substance was deposited. This was filtered out and the filtrate, which now had a beautiful green fluorescence, allowed to stand for some days. There appeared needle-shaped crystals which were red by transmitted light, green by reflected light. These dissolve with some difficulty in alcohol, giving it a light-purple color; easily in concentrated sulphuric acid with a red color; but they are insoluble in alkalies even on boiling. The quantity of crystals was so small as to make an analysis of the compound impossible, but it is in all probability coeruleïn trimethyl ether.

COERULEÏN MONOETHYL ETHER.

This compound was made in the same way as the monomethyl ether, using ethyl iodide and boiling only nine hours.

It was likewise crystallized from alcohol and had all the characteristics of the corresponding methyl derivative. It was dried at 100° C. and the ethoxy group determined, with the following result :

Weight of ether. Gram.	Weight of silver iodide. Gram.	C_2H_5O. Per cent.
0.1313	0.0808	11.81

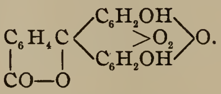
Calculated for $C_{20}H_9O_5(OC_2H_5)$, 12.04 per cent C_2H_5O.

Hence the compound is coeruleïn monoethyl ether.

THEORETICAL.

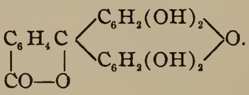
I. GALLEÏN.

The formula for galleïn, as given by Buchka, is



$$\begin{array}{l} C_6H_4C\left\langle\begin{array}{l} C_6H_2OH \\ \qquad >O_2 \\ C_6H_2OH \end{array}\right\rangle O. \\ |\qquad\quad | \\ CO—O \end{array}$$

It is necessary to assume with this formula that oxidation takes place in the process of making galleïn, giving rise to a quinone group. This idea was first suggested to him by the supposed discovery of the so-called hydrogalleïn, which he regarded as a reduction-product intermediate between galleïn and gallin. Hydrogalleïn, according to Buchka, differs essentially from both galleïn and gallin, but gives the same product when acetylized as that obtained from galleïn by acetylization. In order to account for this, he gave galleïn the above formula and to hydrogalleïn the formula :



$$\begin{array}{l} C_6H_4C\left\langle\begin{array}{l} C_6H_2(OH)_2 \\ \\ C_6H_2(OH)_2 \end{array}\right\rangle O. \\ |\qquad\quad | \\ CO—O \end{array}$$

The necessity for providing a formula for hydrogalleïn was the single consideration that led him to assign to galleïn the above formula.

Many attempts were made during the progress of this work to prepare hydrogalleïn and its acetate. The result was always the same—the hydrogalleïn acetate invariably proved to be identical in every respect with gallin acetate. Attempts were made also to make gallol acetate by Buchka's method—reduction of galleïn in acid solution by zinc dust, and acetylization of the product thus obtained. Here again the so-called gallol acetate was identical with gallin acetate. The identity of these three acetates is clearly shown not only by analyses but also by identity of melting-point and by their conduct with sodium carbonate solution, with concentrated sulphuric acid, and with silver nitrate solution. So that no matter whether galleïn be reduced by zinc dust in acid or alkaline solutions, hot or cold, the product is in all cases gallin, which, with acetic anhydride, yields gallin tetracetate. The existence of hydrogalleïn is, therefore, extremely improbable, and it is doubtful if gallol or its acetate has been isolated. The conclusion here stated with reference to hydrogalleïn is in entire accord with Herzig's work, to which reference has already been made.

That galleïn contains a carboxyl group is proved by the fact that it forms esters in the ordinary way. Methyl and ethyl esters have both been prepared. Further, galleïn forms a stable ammonium salt,[1] which suffers no loss of ammonia after prolonged heating, in this respect showing a marked difference from phenolphthaleïn. Galleïn also decomposes sodium, barium, and calcium carbonates, driving out carbon dioxide and forming soluble compounds with the metals. The presence of the carboxyl group may explain, also, why galleïn is converted more easily than other phthaleïns into its corresponding phthalideïn, since there is no lactone ring in this compound. This will be referred to again in the theoretical discussion of coeruleïn.

The formation of the colored tetramethyl and tetraethyl ethers, which are easily saponified to the colorless triethers with alkalies, also proves the presence of a carboxyl group in galleïn. The existence of the blue basic lead salt and of the colored galleïn triphenyl carbamate, which has acid properties, indicates the same thing.

That galleïn contains only three phenolhydroxyl groups is shown by the introduction into its molecule of three phenylisocyanate groups. It has been established, notably by Goldschmidt,[1] that phenyl isocyanate does not react with quinone oxygen, but easily with hydroxyl hydrogen, except when present in carboxyl groups. The galleïn triphenylcarbamate has a color and dissolves in a cold solution of sodium carbonate with color. Hence it must contain a carboxyl group, but cannot be a derivative of gallin (formed by reduction). Since, therefore, galleïn, in free condition, contains one carboxyl and three phenolhydroxyl groups, its structure must be:

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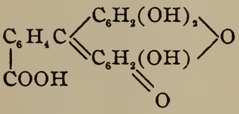
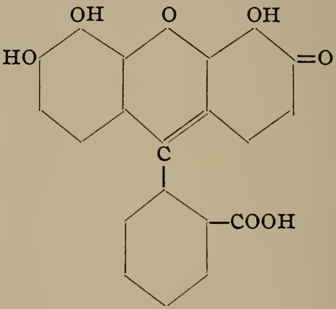
[1] Buchka : Ann. Chem. (Liebig), 209, 263.

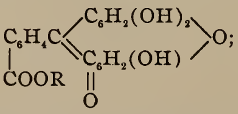


$$\underset{\substack{|\\COOH}}{C_6H_4C}\left\langle\begin{array}{l}C_6H_2(OH)_2\\\underset{\substack{\|\\O}}{C_6H_2(OH)}\end{array}\right\rangle O$$

or

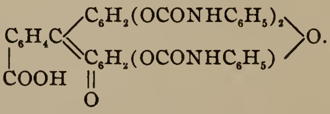


The quinoid structure would explain the deep-red color of galleïn and its solutions. According to this formula the structure of the highly colored methyl or ethyl ester would be



$$\underset{\substack{|\\COOR}}{C_6H_4C}\left\langle\begin{array}{l}C_6H_2(OH)_2\\\underset{\substack{\|\\O}}{C_6H_2(OH)}\end{array}\right\rangle O;$$

and for the colored triphenyl carbamate having acid properties,



$$\underset{\substack{|\\COOH}}{C_6H_4C}\left\langle\begin{array}{l}C_6H_2(OCONHC_6H_5)_2\\\underset{\substack{\|\\O}}{C_6H_2(OCONHC_6H_5)}\end{array}\right\rangle O.$$

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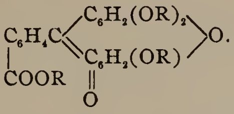
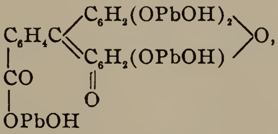
[1] Ber. d. chem. Ges., **22**, 3105.

This formula for galleïn explains also the formation and properties of its colored tetramethyl and tetraethyl ethers. These would be represented thus:



$$\begin{array}{l} \qquad\quad\diagup C_6H_2(OR)_2\diagdown \\ C_6H_4C\Big\langle \qquad\qquad\qquad\quad \rangle O. \\ | \qquad\quad \diagdown\!\!\diagdown C_6H_2(OR)\diagup \\ COOR \quad \| \\ \qquad\qquad\; O \end{array}$$

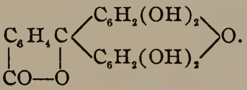
A compound with such a structure one would expect to be colored and to lose one alkyl group by saponification. As a matter of fact these ethers are colored (deep-red), and are saponified by sodium carbonate or hydroxide leaving a trialkyl ether. The deep-blue basic lead salt probably has the following formula:



$$\begin{array}{l} \qquad\quad\diagup C_6H_2(OPbOH)_2\diagdown \\ C_6H_4C\Big\langle \qquad\qquad\qquad\qquad\quad \rangle O, \\ | \qquad\quad \diagdown\!\!\diagdown C_6H_2(OPbOH)\diagup \\ CO \qquad\quad \| \\ | \qquad\qquad\;\; O \\ OPbOH \end{array}$$

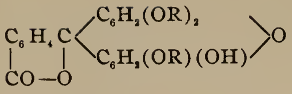
and the blue potassium salt, which is precipitated when a saturated alcoholic solution of galleïn and a saturated alcoholic solution of caustic potash are mixed, probably has a similar structure, the metal potassium replacing the PbOH groups.

There are compounds, however, which seem to be derived from a tautomeric form of galleïn. This would have the lactoid structure and be represented thus:



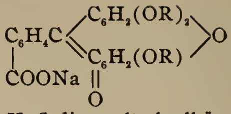
$$\begin{array}{l} \qquad\qquad\diagup C_6H_2(OH)_2\diagdown \\ C_6H_4C\Big\langle \qquad\qquad\qquad\quad \rangle O. \\ | \qquad\; | \quad \diagdown C_6H_2(OH)_2\diagup \\ CO\!-\!O \end{array}$$

To this class belong the trimethyl and triethyl ethers which, when uncombined, are colorless, but dissolve in sodium carbonate with a red color. The relation between the free ethers and their alkali salts appears to be the same as that between phenolphthaleïn and its salts. This relation is shown in the following formulas:



$$\begin{array}{l}C_6H_4C\left\langle\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)(OH)\end{array}\right\rangle O\\ |\qquad\ |\\ CO-O\end{array}$$

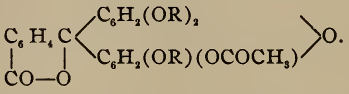
I. Galleïn trialkyl ether.
(Colorless.)



$$\begin{array}{l}C_6H_4C\left\langle\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)\end{array}\right\rangle O\\ |\qquad\qquad\ \ \|\\ COONa\quad\ O\end{array}$$

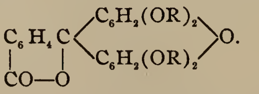
II. Sodium salt of galleïn
trialkyl ether. (Red.)

That Formula I. above, correctly represents the structure of the galleïn trialkyl ethers is indicated further by the fact that they can be readily acetylized as well as transformed into the colorless tetralkyl ethers. The products thus obtained are also colorless. Since the hydrogen atom is replaced by this process, the trialkyl gallein acetate is insoluble in alkalies except on prolonged boiling, which results in saponification of the acetyl group. These characteristics accord with the following structure for the trialkyl gallein acetate,



$$\begin{array}{l}C_6H_4C\left\langle\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)(OCOCH_3)\end{array}\right\rangle O.\\ |\qquad\ |\\ CO-O\end{array}$$

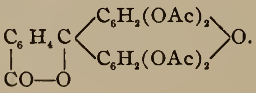
The conception of galleïn as a tautomeric substance finds support also in the existence of two classes of tetralkyl ethers —one, the quinoid (colored), already referred to; the other, the lactoid (colorless), which would have this structure:



$$\begin{array}{l}C_6H_4C\left\langle\begin{array}{l}C_6H_2(OR)_2\\ C_6H_2(OR)_2\end{array}\right\rangle O.\\ |\qquad\ |\\ CO-O\end{array}$$

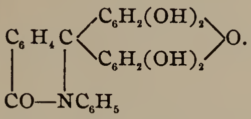
With such a structure one would expect them to be colorless and unaffected by alkalies. Both of these characteristics they were found to possess.

The acetate and the benzoate of galleïn would properly be derived from its lactoid modification, since they are colorless and (at least in the acetate) are known to contain four acid residues. Letting Ac represent the acid residue, they would have the structure



$$\begin{array}{l}C_6H_4C\left\langle\begin{array}{l}C_6H_2(OAc)_2\\ C_6H_2(OAc)_2\end{array}\right\rangle O.\\ |\qquad\ |\\ CO-O\end{array}$$

Galleïn anilide, a colorless compound, made by Albert,[1] should be a derivative of the lactoid modification also and have the structure :[2]



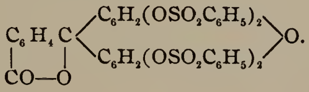
$$C_6H_4C\begin{cases}C_6H_2(OH)_2\\C_6H_2(OH)_2\end{cases}\!\!>O. \quad \text{(ring: } C_6H_4 - CO - NC_6H_5 - C\text{)}$$

The colorless methyl ether which he made from the anilide and called a dimethyl ether is very probably a tetramethyl ether. By combustion-analysis he found carbon = 72.72 per cent, hydrogen = 4.58 per cent.

	Calculated for	Per cent C.	Per cent H.
Di-ether	$C_{28}H_{19}O_6N$[3]	72.25	4.08
Tetra-ether	$C_{30}H_{25}O_6N$	72.70	5.08

From the above it is seen that this compound is more probably a tetraether than a diether.

Another of the lactoid derivatives of galleïn is the tetrabenzenesulphonate described by Georgescu.[4] He gives it the diketone formula which has been abandoned for all phthaleïns. It more probably has the structure



$$C_6H_4C\begin{cases}C_6H_2(OSO_2C_6H_5)_2\\C_6H_2(OSO_2C_6H_5)_2\end{cases}\!\!>O. \quad \text{(ring: } C_6H_4 - CO - O - C\text{)}$$

Galleïn, then, is tautomeric, yielding two classes of derivatives, those with color having the quinoid structure, and colorless derivatives with the lactoid structure. Free galleïn has the quinoid structure.

The formation of the anhydride of pyrogallol ketone and benzoic acid, by fusing galleïn with caustic potash, as described by Buchka, finds a very easy explanation if we adopt the above formula for galleïn. This is shown in the following equation :

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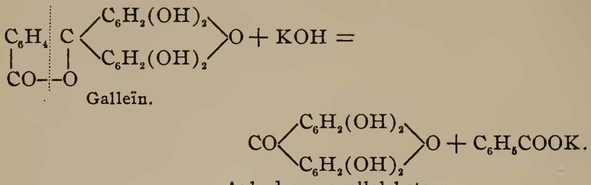
[1] Ber. d. chem. Ges., 27, 2794. The fact that this compound and its methyl ether are colorless makes it certain that they do not contain quinone groups and hence do not have the formulas given them by Albert.

[2] The position of the $>NC_6H_5$ group in this compound has not yet been determined.

[3] This is the formula for the dimethyl ether of galleïn anilide according to Buchka's formula.

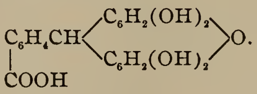
[4] Bulletinul Societatii De Sciinte Fizice d. Bucuresci România, 1, 215.



Galleïn.

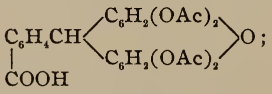
Anhydropyrogallol ketone.

The structure of gallin is established in a measure by its relation to galleïn, from which it is derived by the addition of two atoms of hydrogen. This probably reduces the quinoid group with simultaneous loss of color, and the product is doubtless properly represented thus :

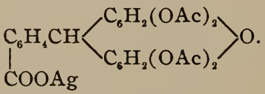


Gallin.

In support of this view of its structure is its easy transformation into the colorless tetracetate, a compound with acid properties. This characteristic the acetate shows not only in dissolving readily in sodium carbonate solution, but also in forming a silver salt. The structure of gallin acetate and its silver salt is shown in the following formulas :

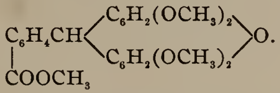


Gallin acetate.



Silver salt of gallin acetate.

A further proof of the correctness of this view of the structure of gallin is the formation of a pentamethyl derivative by the action of methyl iodide upon an alkaline solution of gallin. It probably has the following structure:

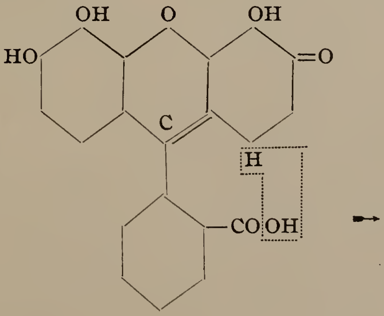


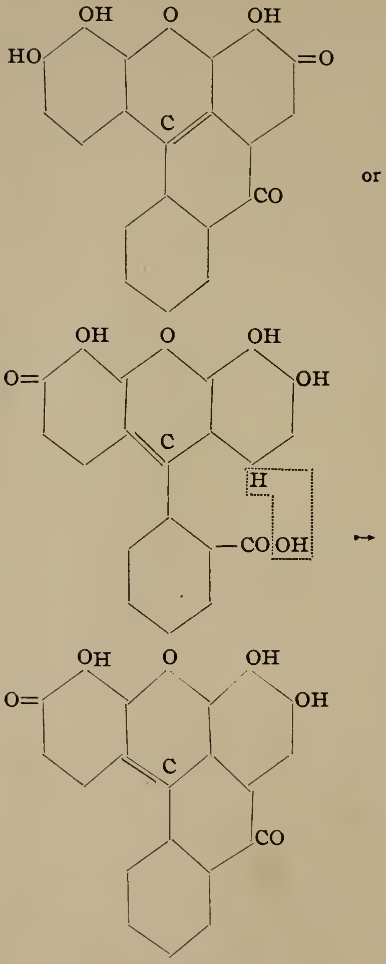
$$\begin{array}{l} \mathrm{C_6H_4CH}\left\langle\begin{array}{l}\mathrm{C_6H_2(OCH_3)_2}\\ \mathrm{C_6H_2(OCH_3)_2}\end{array}\right\rangle\mathrm{O.} \\ | \\ \mathrm{COOCH_3}\end{array}$$

As was to be expected, this ether, though insoluble in cold alkalies, may be saponified by heating in alkali solutions, forming a product easily soluble in sodium carbonate solution without color.

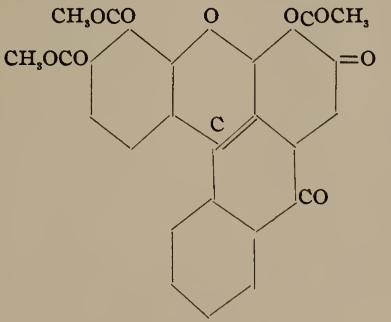
II. COERULEÏN.

Coeruleïn is the phthalideïn of galleïn and sustains to it the same relation that phenolphthalideïn bears to phenolphthaleïn. Baeyer, in his work on phenolphthalideïn, found that when it was distilled with zinc dust, it yields phenylanthracene. Buchka obtained the same product by distilling coeruleïn with zinc dust. Since coeruleïn is derived from galleïn, probably by the loss of one molecule of water, and since, according to Buchka's work, it is a derivative of phenylanthracene, it would seem that the hydroxyl group of the phthalic acid residue in galleïn unites with one of the hydrogen atoms of one of the pyrogallol residues to form water, the readjustment of affinities taking place as represented in the following formulas:

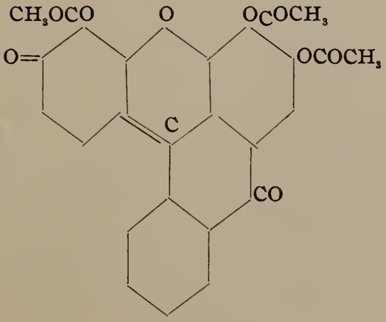



or

That the carboxyl group of galleïn takes part in the reaction is indicated by the fact that, while galleïn is easily soluble in sodium carbonate solution, coeruleïn is insoluble in such a solution. The presence of a carboxyl group in galleïn explains the easy formation of coeruleïn, compared with other phthalideïns. This formula for coeruleïn is also in accord with the fact that when all the oxygen atoms in coerulein are replaced by hydrogen, by means of zinc dust, phenylanthracene is formed. It easily explains how coeruleïn forms a triacetate easily reduced with zinc dust in acetic acid solution. Such a derivative would be represented thus:

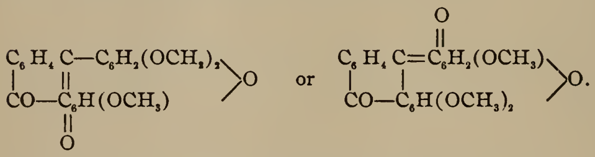


or



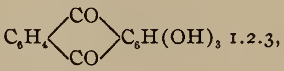
With the formulas given above for coeruleïn there is a possibility of having three varieties of monalkyl ethers. Two monomethyl ethers are described in the experimental part of this paper. It is impossible at present to determine the exact position of the methyl group in these ethers. They are readily soluble in alkalies—a characteristic they could not show if only one hydroxyl group were present in coeruleïn, as represented in Buchka's formula for this compound. Again the fact that there are two monoethers requires that more than one hydroxyl group be present in the molecule.

A methyl ether was made, which was entirely insoluble in alkalies, even on boiling, but in such small amounts as to make analysis impossible. This was probably coeruleïn trimethyl ether. It would have the structure



$$\left.\begin{array}{l} C_6H_4\,C{-}C_6H_2(OCH_3)_2 \\ |\qquad \| \\ CO{-}\underset{\overset{\|}{O}}{C_6}H(OCH_3) \end{array}\right\rangle O \quad \text{or} \quad \left.\begin{array}{l} C_6H_4\,C{=}\overset{\overset{O}{\|}}{C_6}H_2(OCH_3) \\ |\qquad | \\ CO{-}C_6H(OCH_3)_2 \end{array}\right\rangle O.$$

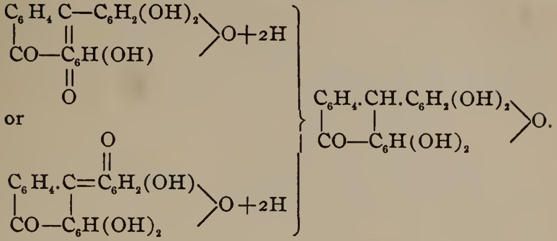
Coeruleïn thus appears as a derivative of anthragallol,



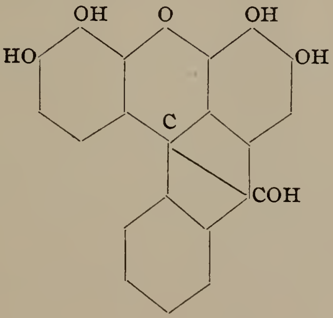
$$C_6H_4\left\langle\begin{array}{c} CO \\ CO \end{array}\right\rangle C_6H(OH)_3 \ 1.2.3,$$

which, like coeruleïn, is soluble in alkalies with a green color. This will explain why coeruleïn resembles alizarin and anthragallol in its property of forming insoluble lakes with chromium, iron, and aluminium mordants. The name, alizarin-green, by which coeruleïn is known, recalls this fact, which has long been known to the dyer. The above formula for coeruleïn also serves to recall the aurin group of dyestuffs, to which it shows certain resemblances.

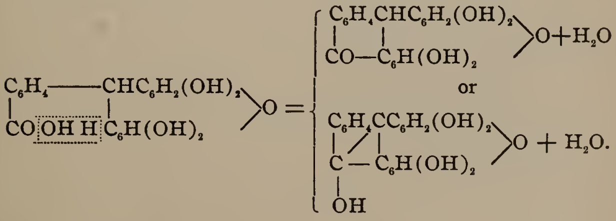
Coerulin is derived from coeruleïn by addition of two hydrogen atoms. This would probably result first in reducing the quinoid group, thus :



The reduced product would be expected to go over to its more stable form and become :



Coerulin is formed also from gallin by the action of concentrated sulphuric acid in the cold. This transformation may be represented thus :



In favor of this view of the structure of coerulin is the fact that it forms a pentacetate with acetic anhydride.

The more important facts brought out in this paper may be found in the following summary:

SUMMARY.

1. The only reduction-product of galleïn by zinc dust, whether in acid or alkaline solution, is gallin.

2. Galleïn forms monoesters, showing that it contains one carboxyl group.

3. Three phenyl isocyanate groups may be introduced into a molecule of galleïn, proving that it contains three phenol hydroxyl groups.

4. Two classes of tetralkyl ethers, colored and colorless, are derivable from galleïn, indicating that it reacts in tautomeric modifications.

5. Galleïn yields a colorless tetracetate, as shown by making determinations of the number of acetyl groups introduced. This proves that galleïn may act as a tetracid phenol.

6. Colorless trialkyl derivatives of galleïn, which resemble phenolphthaleïn, are described.

7. A colorless trimethyl galleïn monacetate is described.

8. Gallin pentamethyl ether and gallin tetracetate furnish evidence as to the structure of gallin.

9. A silver salt of gallin tetracetate also furnishes evidence as to the structure of gallin.

10. Coeruleïn is shown to form a triacetate—by making determinations of the number of acetyl groups introduced.

11. Coeruleïn forms two monomethyl ethers, and a methyl ether insoluble in alkalies; likewise a monoethyl ether.

12. Coerulin forms a pentacetate, as shown by making determinations of the number of acetyl groups introduced.

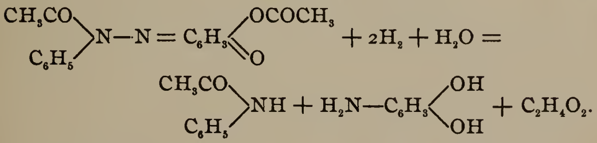
CORNELL UNIVERSITY,
ITHACA, N. Y.,
March, 1901.

ON THE TWO MODIFICATIONS OF BENZENE-4-AZORESORCIN AND THE CONSTITUTION OF THE OXYAZO COMPOUNDS.

BY W. R. ORNDORFF AND E. D. THEBAUD.

In 1887 Will and Pukall[1] found that benzene-4-azoresorcin, $C_6H_5N_2C_6H_3(OH)_2(1,2,4)$, could be obtained in two modifications, one melting at 161° and crystallizing from dilute alcohol in long, reddish-yellow needles, the other melting at 170° and crystallizing from ordinary alcohol in short, dark-red needles. They also found that each modification could be converted into the other at will by using either strong or dilute alcohol as the solvent.

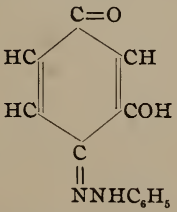
In 1892 Goldschmidt and Pollak[2] showed that the diacetyl derivative of the modification melting at 161° gave, on reduction with zinc dust and acetic acid, acetanilide and amidoresorcin in accordance with the following equation :



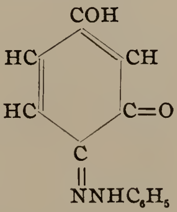
$$\begin{matrix}CH_3CO\\C_6H_5\end{matrix}\!>N-N=C_6H_3<\begin{matrix}OCOCH_3\\O\end{matrix}+2H_2+H_2O=$$

$$\begin{matrix}CH_3CO\\C_6H_5\end{matrix}\!>NH+H_2N-C_6H_3<\begin{matrix}OH\\OH\end{matrix}+C_2H_4O_2.$$

They, therefore, conclude that benzene-4-azoresorcin is a hydrazone quinone and not an oxyazo compound, and that it must have one of the two following formulas, according as it is considered a para- or an orthoquinone derivative :



I.



II.

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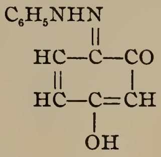
[1] Ber. d. chem. Ges., **20**, 1119.

[2] *Ibid.*, **25**, 1342.

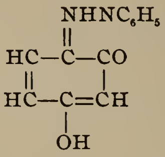
They give the preference to the second formula on account of the easy transformation of the diacetyl derivative into acetanilide and amidoresorcin on reduction, and because the acetyl derivatives of paraoxyazo bodies are only reduced to hydrazo compounds by such treatment.

If this view of Goldschmidt and Pollak be correct, then two stereoisomeric phenylhydrazones of formula II should be possible, as follows:



I.

and



II.

As there are two modifications of benzene-4-azoresorcin, which may be converted one into the other with the greatest ease, it seemed quite likely that we have here to deal with a case of stereoisomerism, such as has been observed already in the case of a number of unsymmetrical phenylhydrazone derivatives. The following investigation was undertaken to test this hypothesis and incidentally to add something to our knowledge of the constitution of the oxyazo compounds.

Benzene-4-azoresorcin was made and purified according to the method of Will and Pukall.[1] It was then recrystallized from 35 per cent alcohol and from ordinary alcohol, and both modifications described by these authors were obtained. The statements made by them in regard to these products were confirmed in every particular. On analysis by the Dafert modification of the Kjeldahl method the products gave the following results:[2]

Weight of substance. Gram.	Weight of NH_3 found. Gram.	Per cent N found.	Calculated for $C_{12}H_{10}N_2O_2$.
0.0924	0.0147655	13.14	13.11
0.0910	0.0145418	13.14	....

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[1] Ber. d. chem. Ges., 20, 1121.

[2] The atomic weights used in this paper are those recommended by the German Chemical Society. See Ber. d. chem. Ges., 31, 2761 (1878).

It has been shown by Hewitt, Moore, and Pitt[1] that many azo compounds contain water of crystallization, which they give up on standing over sulphuric acid in a vacuum-desiccator or on heating in an air-bath to 70°. As the modification of benzene-4-azoresorcin, melting at 161°, is obtained by crystallizing the modification melting at 170° from dilute alcohol, it was thought possible that it might contain water of crystallization, and for this reason melted at a lower temperature. But it was found to lose no weight when kept in a Hempel vacuum-desiccator for forty-eight hours or when heated in an air-bath to 110° to 120° for several hours. Hence the modification melting at 161° does not contain water of crystallization. The modification melting at 170° was then treated in the same way and was also found to lose no weight. It, hence, contains neither alcohol nor water of crystallization.

When recrystallized from benzene both modifications yield only the product melting at 170°.

It was not found possible to determine the molecular weight of the two modifications, owing to the ease with which one form changes into the other, but it is extremely probable, from the method of formation and the remarkable ease with which they are converted into each other, that they are metameric substances and are both correctly represented by the formula $C_{12}H_{10}N_2O_2$. Both modifications give the same diacetyl product, melting at 104°, when heated with acetic anhydride and fused sodium acetate. From these facts it seems highly probable that the two modifications have the same structure and are therefore stereo- or space-isomers, corresponding to the formulas given above. A similar case of stereoisomerism is seen in the two modifications of the phenylhydrazone derivative of salicylic aldehyde, $HOC_6H_4CH = N.NHC_6H_5$, melting at 142° and 104°–105°. The lower melting form is converted into the higher one by warming with alcohol.

We next endeavored to determine whether this stereoisomerism could be shown to exist in the derivatives of benzene-4-azoresorcin. For this purpose the diacetyl product melting at 104° was carefully recrystallized from 35 per cent alcohol.

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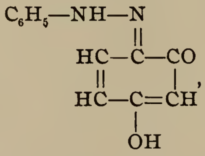
[1] Ber d. chem. Ges., 31, 2114.

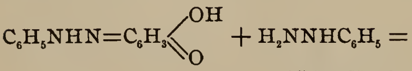
The product obtained melted at 106° and had a reddish-yellow color, whereas the product recrystallized from ordinary alcohol melted at 104° and had a pure yellow color.

The monoethyl ether of benzene-4-azoresorcin was then made and purified according to the method of Will and Pukall.[1] From ordinary alcohol it crystallized in short, brownish-red needles which melted at 87°. When this product was recrystallized from dilute alcohol (35 per cent), it gave long, reddish-yellow needle-shaped crystals, which melted at 88°. Although the difference in melting-point was only 1°, the difference in color was much more marked than in the case of the two modifications of benzene-4-azoresorcin.

If benzene-4-azoresorcin is in reality a phenylhydrazone derivative of an oxyquinone, as held by Goldschmidt and Pollak and as shown in the following formula,



it should react with phenylhydrazine to give a bisphenylhydrazone, thus:



$$C_6H_5NHN{=}C_6H_3\begin{matrix}\diagup OH \\ \diagdown O\end{matrix} + H_2NNHC_6H_5 = (C_6H_5NHN{=})_2C_6H_3OH + H_2O.$$

In order to make this substance we first made a diacetyl product from benzene-4-azoresorcin and dissolved this in glacial acetic acid. An excess of phenylhydrazine was then added and the mixture heated to boiling for a few minutes. On the addition of water a precipitate formed. This was filtered off, washed thoroughly, dried, and recrystallized from benzene. The product thus obtained had a deep-red color, crystallized in rounded grains and melted sharply at 163°. The substance was analyzed by the Dafert modification of the Kjeldahl method and gave the following results:

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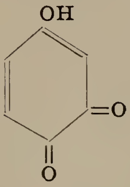
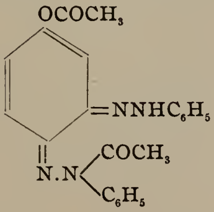
[1] Ber. d. chem. Ges., 20, 1146.

Weight substance. Gram.	Weight of NH_3 found. Gram.	Per cent N found.	Calculated for $C_{22}H_{20}N_4O_3$.
0.0377	0.006615	14.43	14.46
0.0447	0.00784325	14.43	....

The substance is therefore the diacetyl derivative of the bis-phenylhydrazone of the oxyquinone :



and has the following structural formula :

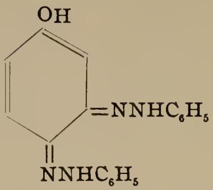


The diacetyl product was then saponified with alcoholic caustic potash, the product precipitated with water, the precipitate washed thoroughly with water and recrystallized from hot dilute acetic acid. The product thus obtained crystallizes in dark-red needles, which melt sharply at 160°. An analysis by the Dafert-Kjeldahl method gave the following result :

0.3941 gram substance gave 0.07132976 gram nitrogen.

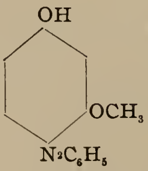
	Calculated for $(C_6H_5—NH.N=)_2(C_6H_3OH)$.	Found.
N	18.45	18.10

The product is, hence, the bis-phenylhydrazone of the oxyquinone and must have the following formula :



It is soluble in caustic potash solution and in hydrochloric acid, in benzene, ether, chloroform, and alcohol, but acetic acid is the best solvent from which to recrystallize it. In concentrated sulphuric acid it dissolves with a reddish-brown color, and on reduction with zinc dust in acetic-acid solution it gives aniline and a product which gives a red color with a solution of bleaching-powder and also with ferric chloride solution. The addition of an excess of caustic potash solution to the acetic acid solution of the reduction-products gave a deep-blue color, which became green on standing, or more quickly on shaking with air. Owing to the extreme instability of this reduction-product it was impossible to isolate it and determine whether it was a diamidophenol or not. Aniline was isolated, however, and identified by its characteristic reactions, and it is probable that the other product was 1,3,4-diamidophenol, as it gave the characteristic color reactions of this substance.

We then tried to prepare the orthomonomethyl ether of benzene-4-azoresorcin.



A monomethyl ether of benzene-4-azoresorcin has already been prepared by Will[1] by the action of caustic potash and methyl iodide on benzene-4-azoresorcin. This author found it extremely easy to make the monoethers, but very difficult to prepare the diethers. From the method of preparation of this monomethyl ether of Will it seems quite probable that it has the following formula:

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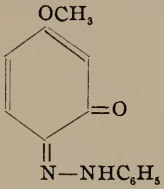
[1] Ber. d. chem. Ges., 21, 604.



This formula would explain very simply the great difficulty Will found in preparing the diethers of benzene-4-azoresorcin.

We prepared this ether by the method of Will. It was a red crystalline product which, when carefully purified by recrystallization from ordinary alcohol, melted at 123° and not at 114°, as given by Will.

The method by which we attempted to prepare the ortho ether was as follows: The monomethyl ether of resorcin, boiling at 243° to 244°, was first prepared and purified according to the method of Tieman and Parrisius.[1] This ether was dissolved in alcohol and treated with the theoretical amount of diazobenzene chloride in dilute alcohol, to convert it into the azo compound. After standing for half an hour the mixture was poured into an alcoholic solution of sodium acetate. A red crystalline product separated out. This was filtered off, washed with water, and recrystallized twice from alcohol. Finally it was recrystallized from a mixture of chloroform and alcohol. The product crystallized in short, red needles, melting at 189° to 190°. Analyses by the Dafert-Kjeldahl method gave the following results:

I. 0.0585 gram substance gave 0.01205476 gram NH_3.

II. 0.0576 gram substance gave 0.01158253 gram NH_3.

	Calculated for	Found.	
	$(C_6H_5N_2)_2C_6H_2\left\langle\begin{matrix}OH\\OCH_3\end{matrix}\right.$.	I.	II.
N	16.90	16.95	16.54

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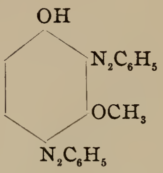
[1] Ber. d. chem. Ges., 13, 2363.

The product is, hence, the monomethyl ether of resorcindisazobenzene. As it is formed under similar conditions to those which gave Kostanecki his resorcin disazobenzene, (2,4), and is soluble in caustic potash solution, it probably has a similar structure:



Contributions from the Sheffield Laboratory of Yale University.

LXXVIII.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.

II.—GRADATIONS IN THE PROPERTIES OF ALUMS.

BY JAMES LOCKE.

In my first paper on this subject[1] I attempted to show that the well-known difficulties which confront the chemist in classifying the elements and their compounds according to the Periodic System are confined practically to the latter class of substances. That there is a definite connection between the properties of an element and those of its compounds is, of course, obvious from the numerous cases in which both fulfil the requirements of the system, But, to take one of the chief difficulties, there are almost no instances in which, when an element can appear in more than one degree of oxidation, the properties of its compounds in each type find accurate interpretation by the System. As a case in point may be cited nitric acid, the nitrates, and nitrous acid and the nitrites, as compared respectively with the derivatives of the pentoxide and trioxide of phosphorus. So far as their oxygen compounds are concerned, the two elements have in neither the quinquivalent nor trivalent state anything in common, except their valence and acid-forming nature. In crystallographic form, solubility, even in formulas, their derivatives are inherently different. Nitrogen pentoxide is a volatile liquid; phosphorus pentoxide a non-volatile solid. The former forms only the monobasic acid, HNO_3; the latter yields preferably polybasic acids. The normal nitrates are in every case readily soluble in water. The normal phosphates, pyrophosphates, and metaphosphates are in almost every case insoluble in water.

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[1] This JOURNAL, 20, 581.

With the trioxides the degree of similarity is about the same—strict analogy is practically absent. But, nevertheless, such a loose periodic system worship prevails, that almost every modern text-book on inorganic chemistry contains a stereotyped statement that nitric acid is analogous to phosphoric acid. In some instances even these bounds have been far overstepped. Probably the most thoroughly systematized smaller work on the subject is that of Professor Ramsay. On pages 333ff of his "System of Inorganic Chemistry" (1891) he classes nitrogen tetroxide with vanadium tetroxide, nitrous acid with vanadious hydroxide. The latter two are apparently analogous because they have the analogous formulas, $NO(OH)$ and $VO(OH)$. If this is enough for chemical analogy, why should not the aluminium compound $AlO(OH)$ be put in the same class? Aluminium and vanadium both form alums, and, as he emphasizes of vanadium hydroxide, both unite with the alkalies. I speak of this, not in criticism of Professor Ramsay's book, but in protest against the all-prevailing tendency to go a-begging for chemical analogy when the system requires it.

The term "chemical character of an element" has two very different meanings. In the first place it denotes the behavior of the element itself, in the free state; in the second, the type of reactions of its compounds. In the latter case we may perhaps use an explanatory prefix, and say, for instance, "the character of *ferric* iron" or of *ferrous* iron. The two terms denote two absolutely different states of matter. When one speaks of ferric iron, the mind involuntarily associates it, not with ferrous iron nor metallic iron, but with the salts of aluminium and trivalent chromium; with two elements which in the free state bear no analogy to metallic iron,[1] and no relation between which and iron is shown by the System. The simplest and most natural analogues of ferric iron are merely the trivalent ions of aluminium and chromium. On the other hand, "ferrous iron" brings to the mind, in addition to the idea of something readily oxidizable, the thought of magnesium and zinc compounds—derivatives of elements which again have nothing in common with metallic iron, and also no resemblance to the metals with which iron in the trivalent state is analogous. Unless a very strong distinction is made between the different usages of the term "chemical character of iron," therefore, this brings about a state of hopeless confusion. Up to the present time it certainly has led to a marked subordination, in importance, of compounds containing elements in unstable states of valence to those in which they are stable. Practically, this is all very well. But from the theoretical standpoint it places a direct obstacle in the way of careful and systematic interpretation of fact, for it makes, in such cases, the power of oxidation or reduction much more important than the simple properties of the compounds as such.

The laws of electricity cease to obtain, as soon as that force has been converted into light, or heat, or chemical energy—no matter which. But ferric iron and ferrous iron are just as distinct primary forms of matter as these are distinct forms of energy. Like the latter, they may be converted, the one into the other, or they may be converted into metallic iron. But whether a ferric salt passes into a ferrous salt, or into metallic iron, the form of matter analogous to aluminium in the combined state ceases to exist. What it becomes, and how readily it undergoes alteration, are questions common to all the ferric compounds, and should be theoretically regarded as belonging to a set of problems entirely distinct and separate from those involving the individual salts.

In order clearly to characterize an element in a given degree of oxidation, the first step should be, not to ascertain how stable or unstable its compounds are, but how nearly they approach, in their physical properties, solubility, etc., the corresponding salts of other elements of the same valence. Such arbitrary conditions as, for instance, the presence of oxygen in working with easily oxidizable substances, should be avoided. And, furthermore, the questions of analogy should be decided along strict lines. The rare-earth metals are, more often than not, spoken of as analogous to aluminium. But the two notable properties which characterize the aluminium salts—the extremely weak basicityof the hydroxide, with the corresponding readiness to form basic salts, and the marked tendency to form complex ions (still more highly developed in chromium and ferric iron), as illustrated in the behavior of aluminium solutions containing oxalic, tartaric, or other organic acids,—are just the reverse of the properties which characterize the strongly basic rare earths. In Dammer's Handbuch we find specific mention of fourteen derivatives of aluminium chloride. Under cerous chloride—the chlorine compound of the best investigated rare earth, we find but two.[1] Barium chloride and cupric chloride show a similar difference. In both cases the divergence is due to very much the same cause. The very nature of the strongly basic ions of barium and cerium prevent the formation of such derivatives; and since the divergence in the behavior of the chlorides is duplicated in that of sulphates, nitrates, bromides, and countless other salts, it surely indicates a radical distinction in the character of cerium and aluminium, to which much more weight should be attached than to the fact that the hydroxides of both are flocculent precipitates. The latter resemblance is essentially the basis of assertions that they are analogous. Cerium may be regarded as the prototype of the rare-earth metals; aluminium as that of trivalent chromium, manganese, vanadium, iron, cobalt, and others. In each group the reactions of these typical metals are closely followed by all their respective members in a way which proves that the separate reactions of each are not to be regarded as individual functions of the elements, but closely correlated with one another. For instance, it means that a trivalent metal which forms alums will yield complex tartrate ions, and that a trivalent metal whice has a strongly basic hydroxide will form an insoluble oxalate, and not form an alum nor a double chloride with potassium chloride, but that its oxide will dissolve readily in dilute acids.

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[1] By this I mean the strong analogy which is exhibited between free elements belonging to the same family and sub-group in the System; for example, metallic zinc nd cadmium, silver and gold, arsenic and antimony, etc.

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[1] Exclusive of the platinichloride, etc.

As illustrations in the above, I have chosen the trivalent metals by chance. Others would have done just as well. If we compare the solubility relations and, exclusive of those in which a change of valence takes place, the reactions, of cuprous compounds, with those of the corresponding silver salts, we find an almost exact similarity between the two. But to ascertain experimentally in how far the strict classification of the elements in the manner indicated is possible, the trivalent metals are especially suitable. Among the alum-forming elements we find one (cobalt) which in the trivalent state yields compounds that are very unstable because of the high valence; and a second one (vanadium) whose compounds are equally unstable because of the abnormally low valence. The range of the atomic weights of the alum-forming trivalent metals, from 27 (Al) to 114 (In), is also exceptionally great for an isomorphous series, and these elements constitute members of six out of the eight families in the system.

The total number of trivalent elements entering into the compounds $M^IM^{III}(SO_4)_2.12H_2O$ is eight: aluminium, titanium, vanadium, chromium, manganese, iron, cobalt, gallium, and indium. Of univalent elements, M^I represents five: sodium, potassium, rubidium, caesium, thallium; and also the ammonium, hydroxylammonium, methylammonium, etc., radicals.[1]

A cursory glance over the literature shows at once that there is a more or less pronounced decrease in stability with increasing atomic weight of the trivalent metal in an alum, and apparently that the heavier the univalent metal the greater will be the stability. Thus, sodium enters into alums only with the lightest of the trivalent metals—aluminium, vanadium, and chromium. The only stable potassium alums are those of aluminium and chromium; potassium-ferric and potassium-gallium alums break down into basic salts very readily, and the only double sulphates of potassium and indium which can be obtained have the formulas

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[1] The existence of the silver aluminium alum described by Church and Northcote is denied by Retgers.

$$KIn(SO_4)_2.4H_2O \quad \text{and} \quad K_2SO_4.2In_2(SO_4)_3.6H_2O.$$

The only alums which have as yet been obtained of titanium are those in which the univalent metal is caesium or rubidium.[1] After much doubt had been cast upon the existence of the manganese alums described by Mitscherlich, Piccini has shown that at least the caesium compound of this element can be easily obtained.[2] Owing to the great instability of their salts, and the correspondingly slight value which could be attached to measurements of their physical constants, I have felt it useless to include these metals in the present investigation, which covers, however, alums of all the other trivalent metals mentioned above, except gallium.

I have also rejected the salts of the substituted amines, as involving the ulterior question of the influence of complex radicals. The ammonium alums, however, in view of their frequent occurrence, have been carefully studied, in order to ascertain how far the generally greater readiness of this complex to yield double salts, as compared with that of potassium, is capable of exact determination. The univalent groups studied, therefore, were sodium, potassium, ammonium, rubidium, caesium, and thallium. For the necessary rubidium and caesium material I am indebted to Professor H. L. Wells, who kindly placed some very pure compounds of these metals at my disposal. The pairings given in the following table were made :

	Al = 27.	V = 51.1.	Cr = 52.1.	Fe = 56.	Co = 59.	In.
23	Na	...	Na	...	...	...
39	K	K	K	K	...	...
..	NH_4	NH_4	NH_4	NH_4	...	...
85	Rb	Rb	Rb	Rb	Rb	Rb
133	Cs	Cs	Cs	Cs	Cs	Cs
204	Tl	Tl	Tl	Tl	...	

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[1] Piccini : Ztschr. anorg. Chem., 17, 355. I have obtained indications of the existence of that of potassium.

[2] Ztschr. anorg. Chem., 17, 355 ; 20, 12. Since this article was sent to press, the remaining manganese alums have also been described by Christansen, and Piccini has obtained those of rhodium.

Solubility in Water at 25°.

As a criterion of the properties of these compounds, their solubility in water at 25° was first determined. The literature contains data only upon the solubility of the compounds of aluminium[1] and vanadium[2] and all those given seem to be of more or less doubtful character, the results having in each case been obtained without the use of a thermostat. In addition to this fact, the actual temperatures chosen by different experimenters for their determinations were rarely identical; so that their results for a given degree would have to be calculated by interpolation. I have accordingly been forced to make new measurements in each case.

The determinations were made in two-ounce bottles, containing water and the finely divided salts in excess. These were placed in a digesting-bath, as described by Noyes,[3] and rapidly shaken by means of a turbine for from four to six hours. The bottles were then placed upright in the bath and the suspended salts allowed to settle for two hours. Throughout the whole time the temperature of the bath was controlled by a gas-regulator; and its variation, in the determinations used below, never exceeded ±0.2°. From 3 to 8 cc. of the supernatant solutions were then transferred by means of a pipette, the bulb of which had been warmed, to small weighing glasses, weighed, and evaporated to dryness. The amounts of the dissolved salts were then determined by heating for four hours at about 200°, at which temperature they became fully dehydrated. The accuracy of this method was first ascertained by experiments made with a variety of alums. In these a weighed quantity of the salt was dissolved in a few cubic centimeters of water, evaporated to dryness, and heated to constant weight. The water was added to ascertain whether an error would be introduced through the formation of basic salt. The following are some of these determinations:

0.4513 gram $CsCr(SO_4)_2.12H_2O$ gave 0.2858 gram anhydrous salt; calculated, 0.2869 gram.

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[1] Poggiale: Ann. chim. phys., (3), 8, 467; Setterberg: Ann. Chem. (Liebig), **211**, 100; Mulder: Scheidekund Verhand., 1864, 91, etc.

[2] Piccini: Ztschr. anorg. Chem., **13**, 441.

[3] Ztschr. phys. Chem., **9**, 606.

0.3540 gram $CsFe(SO_4)_2.12.H_2O$ gave 0.2262 gram anhydrous salt; calculated, 0.2259 gram.

0.2264 gram $CsAl(SO_4)_2.12H_2O$ gave 0.1411 gram anhydrous salt; calculated, 0.1403 gram.

0.7814 gram $TlCr(SO_4)_2.12H_2O$ gave 0.5473 gram anhydrous salt; calculated, 0.5474 gram.

The solubility determination of the vanadium alums required great caution, owing to the readiness with which they undergo oxidation. These salts, which were made according to Piccini's directions,[1] by electrolysis, were washed by decantation with boiled water containing carbonic acid, in the vessel in which they had been recrystallized; and were then brought directly into the bottles, without having been exposed to the air for an appreciable length of time. The water used for their solution had previously been boiled and carbon dioxide led through it in the bottles. The resulting solutions were in this case analyzed by the titration of weighed quantities according to Browning's method.[2] The alums of cobalt, of which only the potassium and ammonium compounds had been described hitherto,[3] unfortunately decompose quite rapidly in solution, giving off oxygen, and determinations could therefore not be made with them. My supply of indium, also, was too small to permit a determination of any but its caesium alum. The results obtained with this compound alone, however, sufficiently indicate the rôle of indium as an alum-forming element.

The results given below are in about half the cases averages of two or more closely-agreeing determinations, and are chosen from the total number made as having been obtained under the most perfect conditions of temperature, etc. The values refer to the number of parts of salt dissolved in 1 liter of water, and in the successive tables M^I represents the univalent metals contained in the alums of the trivalent metal M^{III}.

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[1] Ztschr. anorg. Chem., 9, 106.

[2] *Ibid.*, 1, 158.

[3] Proc. Roy. Soc. (Edinburgh), 59, 760.

	M^I = Na.	K.	NH_4.	Tl.	Rb.	Cs.
M^{III} = Aluminium. At. wt. = 27.						
Anhydrous salt	...	72.3	91.9	75	18.1	4.7
Hydrated "	...	138.4	191.9	117.8	31.5	7.6
M^{III} = Vanadium. At. wt. = 51.1.						
Anhydrous salt	...	...	316.9	256	57.9	7.71[1]
Hydrated "	...	...	785	433.1	99.3	13.1
M^{III} = Chromium, At. wt. = 52.1.						
Anhydrous salt	...	125.1	107.8	104.8	25.7	5.7
Hydrated "	...	243.9	212.1	163.8	43.4	9.4
M^{III} = Iron. At. wt. = 56.						
Anhydrous salt	Does not exist	Basic salt separated	441.5	361.5	97.4	17.1
Hydrated "	...		1244	646.0	169.8	27.2
M^{III} = Indium. At. wt. = 114.						
Anhydrous salt	Does not exist	Does not exist	...	...	...	75.7
Hydrated "			...	...	...	117.3

The sodium alums known dissolve in much less than their own weight of water, and were therefore unsuitable for exact determinations. A sodium alum of iron could not be obtained. With regard to the effect of the univalent metals upon the solubility, it is seen that the higher the atomic weight of an alkali metal, the less soluble is its alum with any given trivalent metal. The solubilities of both the ammonium and thallium compounds, however, lie between those of the corresponding salts of potassium and rubidium. The salt $NH_4Al(SO_4)_2.12H_2O$ forms the only exception to this rule. It is somewhat more soluble than $KAl(SO_4)_2.12H_2O$.[2] The thallium alums, furthermore, are in each case somewhat less soluble than those of ammonium.

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[1] Piccini obtains the same order for the solubility of the vanadium alums at 10°. Expressed in parts by weight of the salts dissolved in 100 parts water, his determinations are as follows :

V—K.	V—NH_4.	V—Tl.	V—Rb.	V—Cs.
198.4	39.76	11.96	2.56	0.464

[2] In Poggiale's determinations this ammonium alum was found to be less soluble than the potassium salt. His results for the latter correspond almost exactly with mine for the ammonium salt, and those for the ammonium alum with mine for that of potassium. It is probable that the coincidence is due to a false arrangement of his tables.

The key to the effect of the trivalent elements upon the solubility relations is given in the failure of any beyond vanadium to form alums with sodium, and in the decomposition of the potassium-ferric salt by water. As this would indicate, the solubilities of the alums of the successive trivalent metals with a given univalent metal increase steadily from aluminium to indium. From what one can judge through the literature, gallium alums also follow this rule being, next to those of indium, the most soluble. The chromium alums alone form an exception. Their behavior will be touched upon at a later point.

In the following table I give the solubilities of all the alums determined, expressed in gram-molecules of the anhydrous salts per liter:

	M^I.	K.	NH_4.	Tl.	Rb.	Cs.
$M^{III} =$	Al	0.28	0.387	0.177	0.059	0.013
	V	...	1.210	0.573	0.177	0.0204
	Cr	0.441	0.407	0.212	0.078	0.0151
	Fe	...	1.659	0.799	0.293	0.045
	In	...	...	...	...	0.172

These results may be represented graphically as a function either of the molecular weight of the respective alums of given trivalent metals, which is virtually the same thing as if they were plotted according to the atomic weights of the univalent metals, but introduces the ammonium salts; or they may be referred to the atomic weights of the trivalent metals. To show the influence of both the univalent and trivalent metals, I give in Figs. I and II the results obtained by each method. In Fig. I the solubilities are plotted as functions of the molecular weights, the univalent metal being the variable. Each broken line, therefore shows the relation between the solubilities of the alums of a given trivalent metal.

As is seen, the curves are in general of the same nature, but they have no uniformity of position, and render no gradation in the solubilities of the alums visible. This is true whether we include the ammonium salts or not, or in other words, whether the solubilities be referred to the molecular weights or to the atomic weights of the univalent metals.

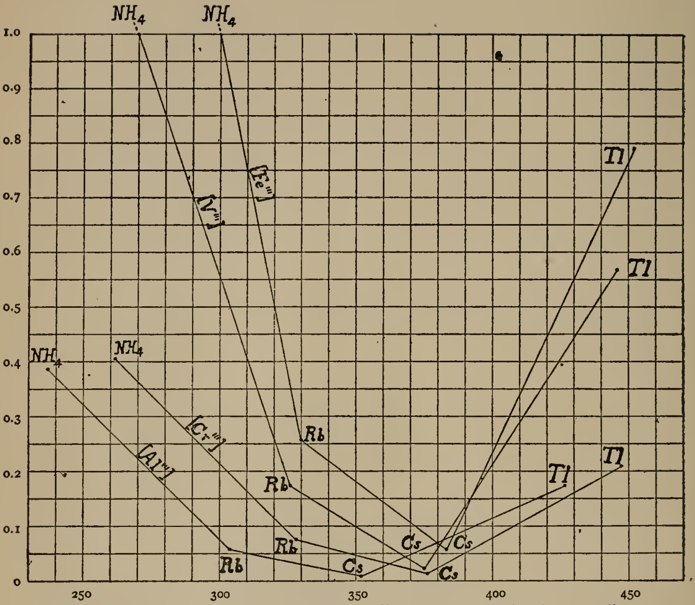

Fig. I.—Abscissae = molecular weights; Ordinates = gram-molecules per liter.

The only influence which the univalent metals or radicals exert is a specific one. The caesium salts are in all cases the least soluble, the rubidium salts next, but the comparatively great solubility of the thallous compounds—which, according to the gradations observed in the case of the compounds of the alkali metals proper, should be the least soluble of all—prevents any satisfactory representation of the solubilities as a function of the atomic weights of the univalent metals.

This specific influence of the univalent metals is readily seen in Fig. II, in which the solubilities are plotted as a function of the atomic weights of the trivalent metals.

As we pass from the caesium compounds through those of rubidium and thallium to the ammonium alums, the difference

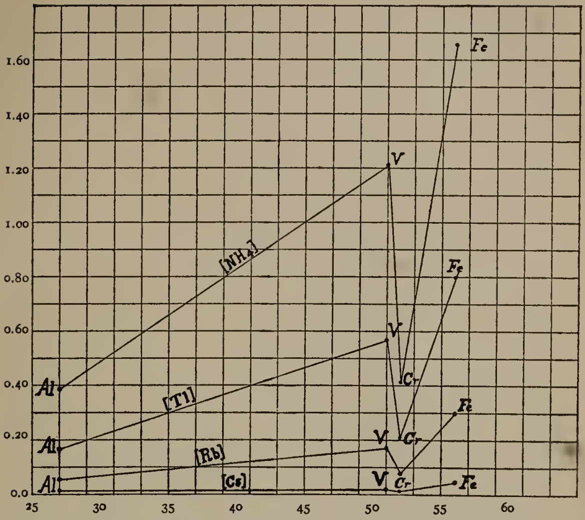

Fig. II.—Abscissae represent atomic weights, ordinates solubilities, expressed in gram-molecules per liter of water. The symbols in brackets indicate in each case the univalent metallic constituent of the alum. Each curve therefore shows the relation between the alums of a given univalent metal with the different trivalent metals

in solubility of the successive salts of a given trivalent metal becomes greater. The increase is also the greater, the heavier the trivalent metal; the result being that while the caesium alums of all the trivalent metals differ only slightly in solubility, and their curve has, therefore, a nearly horizontal position, the curves of the remaining univalent radicals successively become more inclined,[1] the whole effect being somewhat that of an opening fan. But in each case the curves show a sharp break at the chromic compounds; slight in the caesium curve, but more pronounced with each successive univalent metal. Apparently, since the chromic salts accordingly fail to fall properly within the series of gradations with increasing atomic weight of the trivalent metal, the conclusion might be drawn that the great readiness with which this element forms alums is actually an abnormal property. I believe, however, that this is a very loose way of interpreting the fact. Abnormal things do not occur in nature. In the increasing solubility of the chromic alums, as we pass from caesium to ammonium, they show exactly the same mutual relations as are shown by the alums of aluminium, vanadium, or iron. They are perfectly normal in everything except that their behavior is not expressed, like that of the other trivalent metals, by the atomic weight of the metal they contain. And this fact indicates almost positively that *the properties of the compounds are not a function of the atomic weight of the element.* If they were, chromic alums would have about twice their actual solubility.

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[1] Prof. Horace L. Wells suggests to me that the marked difference shown here between the solubilities of the rubidium and caesium alums of iron might have a practical bearing upon the technical separation of rubidium and caesium. At present this is usually effected by the fractional crystallization of their aluminium alums. By using the ferric compounds it would probably be much more perfect.

I do not mean by this to make a sweeping denial of all analogy shown in the Periodic System. Whatever the determining cause of the properties of compounds may be, it is certainly commensurable, in a great many instances, with the atomic weights. But our progress toward the systemization of the compounds will be slow indeed, if we refuse to recognize that Mendeléeff's Law is but a slight approximation of the truth. The abnormal behavior of the thallium alums, according to the Periodic System, might be conventionally explained by the position of thallium as not being a member of the first family of the table ; but in the case of chromium such an explanation is totally inapplicable. The elements aluminium, vanadium, iron, and cobalt[1] constitute members of three different families, and, nevertheless, their alums show a satisfactory gradation according to the atomic weights of these elements. Their alums are merely intermediate members in the series of which the end members, the aluminium, gallium, and indium salts, are so conspicuous because they are compounds of three elements in the same family in the system and thus exhibit the gradations required by the latter.

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[1] The effect of this element upon its alums is shown by their melting-points, as will be described later.

The chromic alums, the thallous alums, and the ammonium alums, respectively, exhibit in each case the same peculiar relations to one another as do the alums of their kindred elements with normal behavior. In the case of the ammonium alums this is especially important, for it shows that whatever the determining cause of the properties of the alums may be, *exactly the same cause must be ascribed to the behavior of the ammonium salts as to that of the alums containing only metals;* and since the ammonium radical has no true atomic weight, therefore, that the atomic weight itself is not the determining cause in the case of any alums whatsoever.

It is an interesting fact that the molecular volumes of the alums, when arranged according to their ascending values, bring both the trivalent and univalent elements into the same order as do their solubilities. In the following tables[1] the molecular volumes are given as calculated from Soret's determinations, with the double formulas, $M^I_2SO_4.M^{III}_2(SO_4)^3.24H_2O$ as the basis of the molecular weights. The solubilities are expressed in gram-molecules per liter:

	$M^{III} = Al$.		$M^{III} = Cr$.		$M^{III} = Fe$.	
	Molecular volume.	Solubility.	Molecular volume.	Solubility.	Molecular volume.	Solubility.
$M^I = K$	546.9	0.28	550.8	0.441	....	....
NH_4	555.9	0.387	557.6	0.407	562.8	1.659
Tl	566.6	0.177	557.7	0.212	560.2	0.799
Rb	562.2	0.059	561.7	0.079	573.3	0.293
Cs	579.2	0.013	581.8	0.015	579.3	0.045

	$M^I = Cs$.		$M^I = (NH_4)$.	
	Molecular volume.	Solubility.	Molecular volume.	Solubility.
$M^{III} = Al$	578	0.013	555.9	0.387
Cr	582	0.015	557.6	0.407
Fe	579	0.045	562.8	1.659
In	584	0.172	....	....

The coincidence, while not absolute, shows that there is a close connection between the molecular volumes of the alums and their solubility. The variations, furthermore, lose much in weight in the fact that a very small error in the determination of the specific gravity is greatly multiplied in the quotient

$$\frac{\text{molecular weight}}{\text{specific gravity}}.$$

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[1] Soret: Arch. sc. phys. Nat. (Genève), (3), 12, 553, etc.; Arzruni: Physikalische Chemie der Krystalle (1893), p. 130. Soret's original article is not at my disposal.

Solubility at Different Temperature.—The next question to be decided was whether there is any regularity in the effect of increasing temperature upon the solubility of different alums. Here I was much limited in my choice of salts, inasmuch as the ferric compounds break down into basic salts when treated with pure water at higher temperatures, and the chromic compounds pass into their green modifications at about 50°. This behavior of the ferric alums prevented the comparative study of any but the rubidium and caesium compounds. As I wished merely to find the general direction of the solubility curves, I did not carry out determinations at temperatures below 25°. Experiments on chromic salts showed that even at 45° they became slightly green on prolonged digestion, and 40° was therefore taken as the upper limit. The following table gives the solubilities of the rubidium and caesium alums of aluminium, chromium, and iron, at intervals of 5° between these limits :

	Rb-Al.		Rb-Cr.		Rb-Fe.	
	Parts per liter.	Gram-mol. per liter.	Parts per liter.	Gram-mol. per liter.	Parts per liter.	Gram-mol. per liter.
25°	18.1	0.059	25.7	0.079	97.4	0.294
30°	21.9	0.072	31.7	0.096	202.4	0.617
35°	26.6	0.087	41.1	0.128	....[1]	....
40°	32.2	0.106	59.7	0.181	....	....
	Cs-Al.		Cs-Cr.		Cs-Fe.	
25°	4.7	0.013	5.7	0.015	17.1	0.045
30°	5.89	0.0167	9.6	0.025	25.2	0.066
35°	7.29	0.0207	12.06	0.032	37.5	0.099
40°	9.00	0.0256	15.3	0.0405	60.4	0.156

Fig. III shows the curves corresponding to the solubilities of these salts expressed in gram-molecules per liter. To facilitate comparison, the solubility curves of the rubidium salts are dotted.

There seems here to be no marked connection between the various alums with respect to the univalent metals, the curve of $CsFe(SO_4)_2$ crossing that of $RbAl(SO_4)_2$ at about 34°. But if we compare the alums, first of caesium, and then of rubidium, we see that the more soluble the alum of a given

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[1] Basic salt formed.

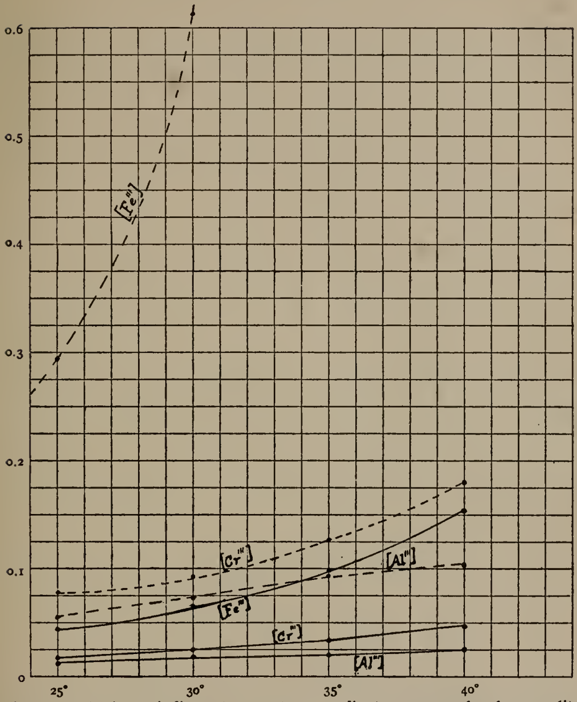

Fig. III.—Abscissae indicate temperatures, ordinates gram-molecules per liter. Symbols in brackets indicate in each case the trivalent metallic constituent of the alum. Curves of rubidium salts are dotted, those of caesium salts solid.

univalent metal is at 25°, the more rapidly does its solubility increase with the temperature. This is marked even in the case of the caesium salts of aluminium and chromium, the solubilities of which at 25° are almost the same (0.013 and 0.015 gram-mol.). The curve of $RbFe(SO_4)_2$ could be followed only to 30°, as at 35° a sparingly soluble basic salt separated from the solution; and the extreme difference in solubility shown for the interval 25° to 30°, may in part be ascribed to a hydrolytic action.

Melting-points.—The melting-point of a hydrated salt is, of course, intimately connected with its solubility, so that in studying them one would expect results approximately analogous to the above. But at the same time I was enabled, in this way, to examine a greater variety of alums, including those of cobalt, the solubility of which could not be determined, the rubidium-indium salt, and the potassium-vanadium and potassium-ferric compounds.

The cobaltic salts examined were those containing rubidium and caesium. These were made in the same way as Marshall[1] obtained the ammonium and potassium cobaltic alums, by the electrolytic oxidation of cobaltous sulphate and addition of the calculated amount of the salts of the desired alkali metal. Both compounds came down in coarse crystalline grains, which could be readily washed by lixiviation with cold water. They were sufficiently stable to permit of rapid drying in the air, but on standing for any length of time they lost oxygen and yielded cobaltous sulphate. The rubidium alum decomposed in this manner, even in a sealed specimen-tube, on standing for a few months. The caesium compound, however, when preserved in the same way, has still retained its green color, thus forming an interesting example of the greater stability of caesium double salts over those of rubidium. Both compounds crystallized in glistening microscopic octahedrons. In view of their marked physical properties, it was not deemed necessary to submit them to a full analysis, but as a matter of general precaution, a weighed quantity of each was ignited below a red heat and the amount of the residual cobaltous and alkali sulphates determined.

0.0683 gram $RbCo(SO_4)_2.12H_2O$ gave 0.0361 gram $Rb_2SO_4 + CoSO_4$; calculated, 0.0357 gram.

0.7004 gram $CsCO(SO_4)_2.12H_2O$ gave 0.2962 gram $Cs_2SO_4 + CoSO_4$; calculated, 0.2959 gram.

The determination of the melting-points was carried out in sealed capillary tubes, of various diameters, and about 2 inches in length. The tubes were in each case filled to somewhat over half their height with the powdered salts. At least five determinations were made with each compound, and samples from several different preparations used for each. Variations in the manner of heating, etc., introduce comparatively large errors in the melting-points, which are in no case very sharp. But after some practice I was able, by carefully following one method of procedure, to reduce the error to about 1°; and in cases where two alums melted at about the same point, as the NH_4–Al(95°) and NH_4–Cr(94°) salts, comparative determinations were made side by side in the same experiment. So, while I make no pretence to great accuracy in these determinations, the errors involved are at least about the same for each compound, and thus the data given below are not vitiated for the purpose of comparison.

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[1] Proc. Roy. Soc. (Edinburgh), 59, 760.

The literature contains various notices on the melting-points of aluminium and chromium alums, and Piccini also determined approximately those of the vanadium salts with sodium (9°), potassium (20°), and ammonium (50°). The last I find to melt at 45°, and for vanadium-potassium alum I have obtained data anywhere from 20° to 28°. The purification of this compound is so difficult that a constant melting-point cannot be observed. My results on the aluminium alums correspond fairly well with those of Erdmann,[1] though being slightly higher, and both his and mine are much higher than those determined by Tilden.[2]

	Na–Al.	K–Al.	NH_4–Al.	Rb–Al.	Cs–Al.
Tilden	61	84°.5	92°	99°	106°
Erdmann	—	92°.5	—	105°	120°.5
Locke	63	91°	95°	109°	122°

Observations on sodium-chromium and caesium-indium alums gave no satisfactory results, the fusion process in each case covering a range of about 10°, and in the case of the indium salt being even then imperfect. My complete results follow :

	M^{III} = Al.	V.	Cr.	Fe.	Co.	In.
M^{I} = Na	63°	(9°)[3]	..	..	..	..
K	91°	(20°)[3]	89°	28°	..	..
Tl	91°	48°	92°	37°	..	..
NH_4	95°	45°	94°	40°	..	(36°)[4]
Rb	109°	64°	107°	53°	47°	42°
Cs	122°	82°	116°	71°	63°	..

[1] Arch. Pharm., **232**, 3.

[2] J. Chem. Soc., **45**, 266.

[3] Piccini: *Loc. cit.*

[4] J. prakt. Chem., [2], **7**, 14.

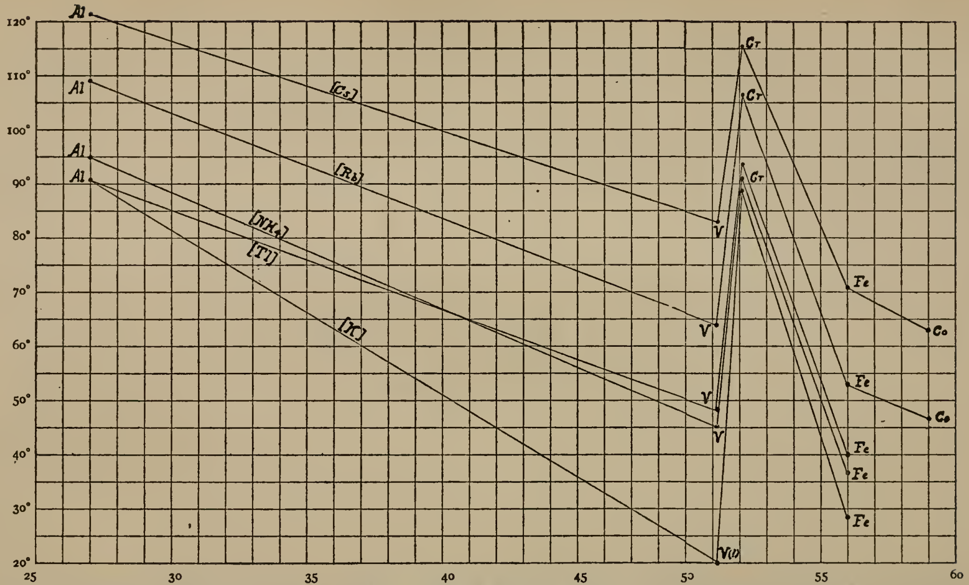

Fig. IV.—Ordinates represent temperatures; abscissae, molecular weights. Symbol in brackets indicates in each case the univalent metallic constituent of the alum.

The order in which the trivalent metals fall, according to the melting-points of their alums with a given univalent metal, is here the same as when determined by the solubility-relations of their salts. The one exception lies in the doubtful melting-point of vanadium-potassium alum, which is a few degrees lower than that of the corresponding ferric salt. The cobalt alums melt at a slightly lower temperature than do the iron compounds, and indium-rubidium alum lower than any other of the rubidium salts, just as the indium-caesium alum is the most soluble member of the caesium series.

With reference to the univalent metals, however, we find the same order as in the solubility tables, so far as the alkali metals are concerned. But the order of the thallium and ammonium series is changed, the thallium salts lying next those of potassium. The vanadium compounds here form the only exception, and in view of their great instability it is to be doubted whether this is not due to unavoidable impurities.

In Fig IV I give the melting-points plotted as a function of the atomic weights of the trivalent metals, R^{III}.

Here, again, we see a sharp break in the case of the chromic salts. The melting-points of the caesium and rubidium alums of aluminium, vanadium, iron, and cobalt are represented by nearly parallel straight lines, which would indicate a very simple relation between them and the atomic weights of these metals. But we must either admit that the values of the melting-points do not depend upon the atomic weights, or that the chromic alums form an exception to a law of nature.

LXXIX.—ON ACETYL AND BENZOYLIMIDODITHIOCARBONIC ESTERS.

By Henry L. Wheeler and Treat B. Johnson.

It has been found in general that, when a thiourethane of the structure —NHCS.OR[1] or —NHCS.SR[2] is treated with alkali and an alkyl halide, imidothiocarbonic esters result.

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[1] Liebermann: Ann. Chem. (Liebig), **207**, 141 (1881); Wheeler, Barnes, Johnson, and Dustin: This Journal, **24**, 60; *Ibid.*, 189; *Ibid.*, 424 (1900).

[2] Fromm and Block: Ber. d. chem. Ges., **32**, 2210 (1899); Busch and Lingenbrink: *Ibid.*, 2620.

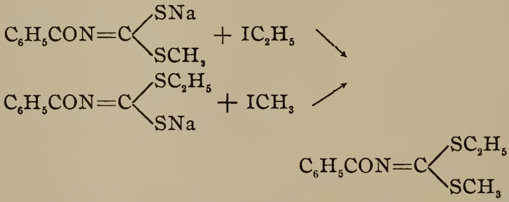
The acyldithiocarbamates form no exception to this rule, although Chaularoff[1] states that he was unable to introduce the ethyl group into ethyl acetyldithiocarbamate,

$$CH_3CONHCS.SC_2H_5,$$

by means of the silver salt and ethyl iodide.

In a previous paper from this laboratory it was shown that, if the urethane is dissolved in alcohol containing sodium ethylate and then treated with ethyl iodide, a good yield of the acylimidodithiocarbonic ester is obtained. This method has now been employed for the preparation of numerous analogues.

Our chief object in examining these compounds has been to determine whether stereochemical isomers are formed when esters with unlike groups are prepared by different methods. For example, methyl ethylbenzoylimidodithiocarbonate (A) might exhibit this sort of isomerism when obtained from sodium methylbenzoylimidodithiocarbonate and ethyl iodide (I) on the one hand, and from sodium ethylbenzoylimidodithiocarbonate and methyl iodide on the other (II).

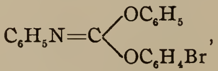


$$\text{I.}\quad C_6H_5CON{=}C\begin{cases}SNa\\SCH_3\end{cases} + IC_2H_5 \searrow$$

$$\text{II.}\quad C_6H_5CON{=}C\begin{cases}SC_2H_5\\SNa\end{cases} + ICH_3 \nearrow$$

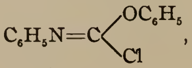
$$C_6H_5CON{=}C\begin{cases}SC_2H_5\\SCH_3\end{cases}\quad (A).$$

A similar question in the oxygen series has already been decided in the negative by Hantzsch and Mai.[2] They showed that phenyl *p*-bromphenylphenylimidocarbonate,



$$C_6H_5N{=}C\begin{cases}OC_6H_5\\OC_6H_4Br\end{cases},$$

whether prepared from the chloride



$$C_6H_5N{=}C\begin{cases}OC_6H_5\\Cl\end{cases},$$

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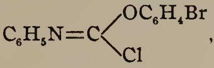
[1] Ber. d. chem. Ges., **15**, 1987 (1882).

[2] *Ibid.*, **28**, 977 (1895).

and sodium *p*-bromphenolate, or from the chloride,



$$C_6H_5N{=}C\begin{cases}OC_6H_4Br\\Cl\end{cases},$$

and sodium phenolate turns out to be one and the same compound.

It was stated by Fromm and Block[1] that they intended to examine this question in the imidodithiocarbonic ester series, but later, in answer to a private communication, Prof. Fromm very kindly replied that he did not wish to reserve this subject for himself, and that, owing to press of other work, he would be very glad to have the question taken up by others.[2]

In order to obtain an idea of the properties of this new class of compounds we first examined a number with simple alkyl groups, and found that, with the exception of dimethylbenzoylimidodithiocarbonate, the lower members of series are oils.

Methyl ethylbenzoylimidothiocarbonate (A, above), prepared in the two ways, proved to be an oil which distilled unaltered at 224° at 20° mm. pressure. No appreciable difference in boiling-point could be detected in the two samples. However, in this case it was possible that in heating one form had been converted into another.

Our efforts were then directed towards obtaining esters that are solid at ordinary temperatures, and many unexpected difficulties were encountered before the desired results were obtained. An account of these difficulties and of experiments in which we obtained mostly degative results, is given here in considerable detail, since it serves to illustrate some peculiar properties of the acyldithiocarbamates or of the acylimidodithiocarbonic esters.

We found that although the dimethyl and dibenzyl imido esters are solids, the methyl benzyl product, prepared in either way, in alcoholic solutions, is an oil which decomposes on distilling at reduced pressure.

When groups with higher molecular weights were selected, we met with a number of cases where solids were obtained but where the desired ester could be prepared in only one way.

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[1] Ber. d. chem. Ges., **32**, 2212 (1899).

[2] Since the above was written Busch has described some samples of stereochemical isomerism in the case of hydrazones of the dithiocarbonic esters. Ber. d. chem. Ges., **34**, 1119 (1901).

The reaction took place smoothly and gave well crystallized products, which could be easily purified, when ethyl chloracetate and paranitrobenzyl chloride were allowed to act on benzylbenzoyldithiourethane, in the presence of sodium ethylate. On the other hand, under precisely similar conditions, the action of benzyl chloride on benzoyldithiourethaneethylacetate, $C_6H_5CO.NHCS.SCH_2CO_2C_2H_5$, and on parabrombenzylbenzoyldithiourethane, and on paranitrobenzylbenzoyldithiourethane, gave oils which in the first two cases showed no signs of crystallizing after standing for weeks.

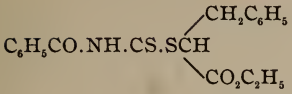
Benzoyl chloride reacted easily and quantitatively with phthalimidoethylbenzoyldithiocarbonate,

$$C_6H_5CO.NHCS.SCH_2.CH_2N(CO)_2C_6H_4\,;$$

but no reaction, in the cold, could be obtained from the sodium salt of benzylbenzoyldithiocarbamate and bromethylphthalimide. When the mixture was heated the sodium salt was decomposed.

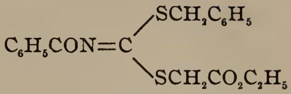
Some of those urethanes which did not act smoothly with benzyl chloride also failed to give the corresponding esters with like groups. It therefore appeared that the difficulty, in these cases, was to be explained by the fact that sodium ethylate decomposed the urethanes (see below).

An attempt was then made to obtain a solid by shaking the aqueous alkaline solution of benzoyldithiourethane ethyl acetate with benzyl chloride. This, in fact, gave a solid which proved to be a sodium salt of a compound structurally isomeric with the product prepared from ethyl chloracetate and benzylbenzoyldithiourethane in sodium ethylate solutions. When this was suspended in water and treated with carbonic acid, a bright-yellow compound was obtained. Although this had precisely the same melting-point as its isomer it was decidedly different in other respects. The bright-yellow color, its solubility in alkali, and the fact that the ester prepared in the other way gave no sodium salt, showed that we had to deal here with a dithiourethane, III, and not an imidocarbonic ester, IV:



$$C_6H_5CO.NH.CS.SCH\begin{array}{l}\diagup CH_2C_6H_5\\ \diagdown CO_2C_2H_5\end{array}$$

III.



$$C_6H_5CON{=}C\begin{array}{l}\diagup SCH_2C_6H_5\\ \diagdown SCH_2CO_2C_2H_5\end{array}$$

IV.

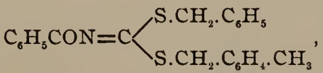
This peculiar result suggests that the methylene hydrogen in compounds containing the complex $—S—CH_2CO—$ will be found to undergo substitution similar to that in desoxybenzoin and benzyl cyanide, although Loven[1] states that he was unable to introduce the methyl group into thiodiglycollic ester by means of sodium alcoholate and methyl iodide. We hope to examine this question later.

It was found that benzylbenzoyldithiourethane forms a fairly stable sodium salt, and from this the dibenzyl carbonic ester, which is characterized by its relatively high melting-point, can be quantitatively obtained. We therefore sought for radicals closely similar to benzyl, and, on employing the metaxyl and mesityl groups, we were finally successful in obtaining solid imidoesters by the two different ways.

Benzylbenzoyldithiocarbonate, sodium ethylate, and metaxylyl bromide reacted in a few minutes and gave a product melting at 97° to 98°.

Metaxylylbenzoyldithiocarbamate, sodium ethylate, and benzoyl chloride reacted after about twelve hours, and gave a product melting mostly at 85° to 86°, but the material did not become clear until 89°.5, and repeated crystallization did not alter this melting-point.

If, instead of using sodium ethylate solutions, the reactions were carried out, in both cases, by shaking in aqueous alkali, the metaxylyl benzylbenzoylimidodithiocarbonic ester,



$$C_6H_5CON{=}C\begin{array}{l}\diagup S.CH_2.C_6H_5\\ \diagdown S.CH_2.C_6H_4.CH_3\end{array},$$

obtained melted precisely at 97° to 98° and the products formed by the two different methhods were identical in every respect.

Although metaxylyl benzoyldithiocarbamate and sodium ethylate do not react smoothly with benzyl chloride, nevertheless with metaxylyl bromide they react in a perfectly smooth manner.

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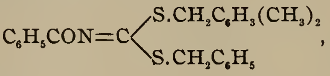
[1] Ber. d. chem. Ges., 18, 3242 (1885).

That the above ester, melting at 85° to 89.°5, contains some impurity or decomposition-product which cannot be separated by crystallizing from alcohol, appears probable, not only from its melting-point but also from the behavior of mesitylbenzoyldithiourethane towards benzyl chloride. It is a curious fact that these substances, in alcoholic solutions, show little tendency to form an imido ester. One-half of the urethane can be recovered unaltered from the alkaline solution after standing twelve hours, the other half is decomposed.

If, instead of using alcoholic solutions, the mesityl urethane is shaken with benzyl chloride and aqueous alkali, the substances react with remarkable ease, the reaction is complete in a few minutes, and the resulting mesityl benzyl ester of benzoylimidodithiocarbonic acid,



$$C_6H_5CON{=}C\left\langle\begin{matrix} S.CH_2C_6H_3(CH_3)_2 \\ S.CH_2C_6H_5 \end{matrix}\right. ,$$

melts at 117°.5.

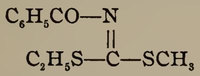
On the other hand, a product identical with this is readily obtained from mesityl bromide, benzylbenzoyldithiourethane and sodium ethylate. These substances react immediately and in a perfectly smooth manner in alcoholic solution.

A somewhat similar difference in tendency to react in alcoholic solutions was observed in the preparation of an imido ester from ethyl α-benzoyldithiourethane propionate, $C_6H_5CO.NHCS.SCH(CH_3)CO_2C_2H_5$, and benzyl chloride, in which case the action was not smooth, while, when prepared in the other manner, from methyl α-brompropionate and benzylbenzoyldithiourethane, a smooth reaction was obtained.

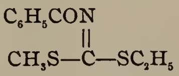
Every reactive halogen compound that has been tried with benzylbenzoyldithiourethane reacts smoothly, while the difficulties encountered in the use of sodium ethylate solutions have been confined entirely to other urethanes. This would indicate that the benzyl urethane is the only one examined that is not decomposed, to some extent, by treating with sodium ethylate. This decomposition of the urethanes will explain most of the negative results, but an explanation for the relative inertness of the urethanes towards benzyl chloride in the presence of sodium ethylate is lacking.

The results show, however, that stereoisomeric acylimidodithiocarbonic esters do not result by the methods in question.

When the acylimidodithiocarbonic esters are treated with amines, mercaptan is evolved, even in the cold, and acylpseudothioureas are smoothly formed. No pseudothioureas of this type have been described, and since they have proved to be quite reactive compounds they will form the subject of a later paper. It is perhaps of interest to note here that when the esters with unlike alkyl groups are treated with aniline, etc., the product obtained is a mixture of two acylpseudothioureas and that both alkyl groups are partially separated as mercaptan. This is not what would be expected if the acylimidodithiocarbonic esters corresponded to a single stable one of the following stereochemical modifications:



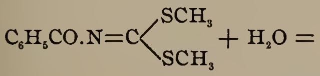
$$\begin{array}{c} C_6H_5CO\text{—}N \\ \| \\ C_2H_5S\text{—}C\text{—}SCH_3 \end{array}$$



$$\begin{array}{c} C_6H_5CON \\ \| \\ CH_3S\text{—}C\text{—}SC_2H_5 \end{array}$$

It appears more probable that the esters in question, consist of mixtures of these two forms.

The behavior of the esters with hydrochloric acid is also in accordance with this view. The symmetrical esters, when gently warmed with acid, undergo hydrolysis and are converted into acylthiolcarbamic esters, as follows:

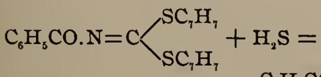


$$C_6H_5CO.N{=}C\begin{cases} SCH_3 \\ SCH_3 \end{cases} + H_2O =$$

$$C_6H_5CO.NHCO.SCH_3 + HSCH_3.$$

Ethyl benzylbenzoylimidodithiocarbonic ester gave a mixture of the two possible thiolcarbamic esters.

When the acylimidodithiocarbonic esters are heated in a stream of dry hydrogen sulphide, mercaptan is given off and the esters are converted into acyldithiocarbamates:



$$C_6H_5CO.N{=}C\begin{cases} SC_7H_7 \\ SC_7H_7 \end{cases} + H_2S =$$

$$C_6H_5CO.NHCS.S.C_7H_7 + C_7H_7SH.$$

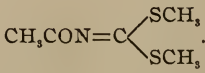
EXPERIMENTAL PART.

Preparation of Acyldithiourethanes.—Most of the primary monothiocyanates unite directly with thiol acids when warmed in benzene solution. As a rule, secondary thiocyanates react less smoothly and many give no dithiourethanes but form products containing sulphur and no nitrogen; 1′-thiocyanethylbenzene, $C_6H_5CH(SCN)CH_3$, and thiocyandesoxybenzoin, $C_6H_5CO—CH(SCN)C_6H_5$, for example. The investigation of the behavior of secondary and tertiary thiocyanates $>$CHSCN and $\equiv$C—SCN with thiol acids is now in progress in this laboratory.

Preparation of Acylimidodithiocarbonic Esters.—In all our experiments the action of sodium ethylate and alkyl halide on the dithiourethanes, at ordinary temperatures and in alcoholic solution, was first tried. When this process gave oils or when a satisfactory reaction was not obtained, the urethanes were dissolved in aqueous alkali and shaken with the halides. In most cases the action of alkali, and especially that of sodium alcoholate, produces a partial decomposition according to the following:

$$C_6H_5CONC(SNa)SR = C_6H_5COSNa + NCSR.$$

This appears to be the chief reaction when the urethanes are treated with sodium in benzene. The acylimidodithiocarbonic ester is then obtained mixed with a thiol ester of benzoic acid and a sulphocyanide, and the sulphocyanide further decomposes into sodium cyanide and a disulphide. Besides this, when sodium alcoholate is used and the formation of imido esters slowly takes place, the latter are partially decomposed with the result that mercaptan is formed which in certain cases also tends to contaminate the products.

Dimethylacetylimidodithiocarbonate, 

$$CH_3CON{=}C\begin{matrix}\diagup SCH_3\\ \diagdown SCH_3\end{matrix}$$

.—This, the first member of the series, was prepared from sodium methyl acetylimidodithiocarbonate and methyl iodide in alcoholic solution. After standing for twelve hours, water precipitated a pale-yellow oil which, when washed and dried, was distilled at 20 mm. pressure. About one-half of the oil boiled below 135° (methyl rhodanide and methyl thiolbenzoate), then the remainder distilled at 135° to 145°. On redistilling, at the same pressure, it practically all boiled at 142° to 144°, and a nitrogen determination in the latter portion of this was made with the following result:

	Calculated for $C_5H_9ONS_2$.	Found.
N	8.58	8.34

Diethyl acetylimidodithiocarbonate was described in a previous paper.[1]

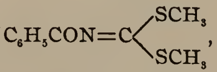
Isoamyl acetyldithiocarbamate, $CH_3CO.NHCS.SC_5H_{11}$.—Isoamyl thiocyanate did not combine as smoothly as the lower rhodanides with thioacetic acid. A portion of the reaction-product solidified, and on crystallizing this from alcohol yellow plates were obtained which melted constantly at 84°. A nitrogen determination gave:

	Calculated for $C_8H_{15}ONS_2$.	Found.
N	6.8	7.0

When this was dissolved in alcoholic sodium ethylate and treated with isoamyl bromide an oil was obtained, about one-half of which boiled below 192° at 20 mm. pressure, (isoamyl thiolacetate and amyl thiocyanate), the remainder distilled at 192° to 205°. On redistilling, at the same pressure, a portion was collected boiling at 198° to 200°. The analysis of this agreed with the calculated percentage for diisoamyl acetylimidodithiocarbonate.

	Calculated for $C_{13}H_{25}ONS_2$.	Found.
N	5.09	5.39

Dimethyl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_3\\SCH_3\end{cases},$$

previously described, and concentrated hydrochloric acid react almost at once. The ester does not dissolve but mercaptan is evolved, and on crystallizing the product from 95 per cent alcohol, colorless needle-like prisms results, which melt at 153° to 154°. When this was mixed with the product which we obtained by heating methyl benzoylthioncarbamate with methyl iodide[1] the melting-point was not altered. The substance is therefore methyl benzoylthiolcarbamate, $C_6H_5CO.NHCO.SCH_3$.

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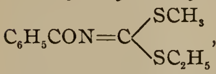
[1] Wheeler and Merriam: *Loc. cit.*

Diethyl benzoylimidodithiocarbonate and hydrochloric acid acted in a similar manner. The product from alcohol melted at 108° and was identical with ethyl benzoylthiolcarbamate, $C_6H_5CO.NHCO.SC_2H_5$, which we obtained from the corresponding diethyl monothiocarbonate and hydrochloric acid.[2]

Methyl ethyl benzoylimidodithiocarbonate,



$C_6H_5CON{=}C\begin{cases}SCH_3\\SC_2H_5\end{cases}$, was prepared from ethyl benzoylimidodithiocarbonate, sodium ethylate and methyl iodide. On distilling the pale yellow-colored oil thus obtained at 20 mm. pressure, it practically all boiled at 224° to 225°.5. Eight grams of the oil were obtained from 13 grams of the urethane. A nitrogen determination gave :

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
N	5.86	6.18

Apparently this same oil was obtained when methyl benzoylimidodithiocarbonate, sodium ethylate, and ethyl iodide were allowed to react. The product in this case boiled at 222° to 224°, the chief quantity boiling sharply at 224° at 20 mm. pressure. When this sample was treated with concentrated hydrochloric acid it readily reacted, but the product, on crystallizing from alcohol, acted like a mixture. It melted at about 120° to 145°, and three crystallizations failed to give a definite melting-point. This material probably consisted of a mixture of the above methyl and ethyl benzoylthiolcarbamates.

When methyl ethyl benzoylimidodithiocarbonate was warmed with aniline a reaction started immediately. The escaping gas was passed into a cooled receiver, and thence into a solution of mercuric cyanide. The oil which condensed in the receiver gave a yellow precipitate with mercuric cyanide, which melted at 66° to 70°. This, therefore, was ethyl mercaptide. The gas which passed into the mercuric cyanide solution produced a grayish precipitate which was difficultly soluble in alcohol and melted at 169° to 170°. This was, therefore, methyl mercaptide.

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[1] This JOURNAL, 24, 201.

[2] *Loc. cit.*

The solid product of the reaction was crystallized repeatedly from alcohol, whereupon it separated in the form of flattened prisms and melted constantly at 79° to 80°. A nitrogen determination gave :

	Calculated for		
	$C_6H_5CO.N{=}C(SCH_3)NHC_6H_5$.	$C_6H_5CO.N{=}C(SC_2H_5)NHC_6H_5$.	Found.
N	10.37	9.86	10.42

The above two acylpseudothioureas were described by Wheeler and Merriam.[1] The product of the action of aniline on dimethyl benzoylimidodithiocarbonate melted at 104°, while that from the diethyl ester melted at 88°. Since the material in the present case is not identical with either of these, and since both methyl and ethyl mercaptan were evolved in its preparation, it follows that this product is a mixture of the two pseudothioureas, which cannot be separated by crystallizing from alcohol. Similar results were obtained by the action of alcoholic ammonia. The product had no definite melting-point and behaved like a mixture.

Di-n-propyl benzoylimidodithiocarbonate, $C_6H_5CO.N{=}CS(C_3H_7)_2$, was obtained as a pale-yellow oil which boiled at 238° to 239° at 20 mm. pressure and a nitrogen determination, for which we are indebted to Mr. J. G. Wild, gave :

	Calculated for $C_{14}H_{19}ONS_2$.	Found.
N	5.01	5.40

Isoamyl benzoyldithiocarbamate, $C_6H_5CONHCS.SC_5H_{11}$.—When molecular quantities of amyl sulphocyanide and thiobenzoic acid were warmed on the steam-bath for twenty-four hours, a thick red oil was obtained which slowly solidified on standing. On crystallizing from dilute alcohol it was obtained in the form of yellow prisms and melted at 48° to 49°.

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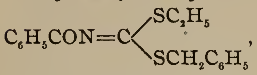
[1] *Loc. cit.*

We are indebted to Mr. W. M. Clark for the following nitrogen determination :

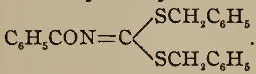
	Calculated for $C_{13}H_{17}ONS_2$.	Found.
N	5.25	5.79

Ethyl benzyl benzoylimidodithiocarbonate,



$C_6H_5CON{=}C\begin{array}{l}\diagup SC_2H_5\\ \diagdown SCH_2C_6H_5\end{array}$, when prepared from the ethyl or benzyldithiourethane, in alcoholic solution, proved to be an oil which could be neither solidified nor distilled without decomposition. The same result was obtained when ethyl benzoyldithiocarbamate was shaken with aqueous alkali and benzyl chloride. Isoamyl benzyl benzoylimidodithiocarbonate prepared from the above isoamyl benzoyldithiourethane showed no signs of crystallizing after standing for several weeks.

Dibenzyl benzoylimidodithiocarbonate,



$C_6H_5CON{=}C\begin{array}{l}\diagup SCH_2C_6H_5\\ \diagdown SCH_2C_6H_5\end{array}$.—When 42 grams of benzyl benzoyldithiocarbamate, 3.4 grams of sodium, in 150 cc. of alcohol and 18.5 grams of benzyl chloride were mixed, a reaction took place almost immediately and the material became semisolid, from the separation of a mass of colorless needles. The reaction was very smooth. On adding water and then crystallizing from alcohol the ester separated in the form of balls of long, colorless, shining, silky needles, which melted sharply at 97° and had an odor which suggested roses or carnations. A nitrogen determination gave :

	Calculated for $C_{22}H_{19}ONS_2$.	Found.
N	3.71	3.81

Paranitrobenzyl benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2C_6H_4NO_2$.—This results smoothly from the rhodanide and thiobenzoic acid, when warmed in benzene on the steam-bath. It crystallizes beautifully from alcohol in clusters of short, yellow needles, which melt at 155° to 156°. A nitrogen determination made by Mr. Clark gave :

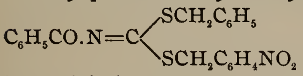
	Calculated for $C_{15}H_{12}O_3N_2S_2$.	Found.
N	8.43	8.11

Parabrombenzyl benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2C_6H_4Br$, prepared from the rhodanide and thiobenzoic acid, did not melt sharply on crystallizing from alcohol. It was dissolved in dilute alkali and precipitated by carbon dioxide, whereupon, on crystallizing from alcohol, it separated as a fine crystalline, yellow powder, which melted at 126°. A nitrogen determination gave:

	Calculated for $C_{15}H_{12}ONS_2Br$.	Found.
N	3.82	4.01

When this was treated with sodium ethylate and benzyl chloride nothing but an oil was obtained which did not solidify after a number of weeks.

Benzyl paranitrobenzyl benzoylimidodithiocarbonate,



$$C_6H_5CO.N{=}C\begin{cases} SCH_2C_6H_5 \\ SCH_2C_6H_4NO_2 \end{cases}$$

, when prepared from benzyl benzoyldithiocarbamate and *p*-nitrobenzyl chloride was obtained as an oil, which, after standing for three weeks, solidified. When this was crystallized from alcohol it formed short needles and melted at 84° to 85°, and a nitrogen determination gave:

	Calculated for $C_{22}H_{18}O_3N_2S_2$.	Found.
N	6.63	6.48

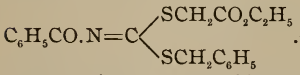
Attempts to prepare this from *p*-nitrobenzyl benzoyldithiourethane and benzyl chloride invariably resulted in the formation of an oil which refused to solidify. The difficulty here is due to the unstable nature of the sodium salt. The nitrourethane dissolves in sodium alcoholate to a deep blood-red solution, and when treated with *p*-nitrobenzyl chloride a red tar is obtained. No attempt was made to prepare this imido ester in aqueous solutions.

Ethyl Acetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH_2CO_2C_2H_5$.—In another article attention was called to the fact that the rhodanethyl acetate of Claesson combines with thiobenzoic acid, smoothly and practically quantitatively, to form a yellow crystalline cake of the above dithiourethane. This substance, therefore, contrary to the statements of Frerich and Beckurts,[1] is not a mustard-oil. On crystallizing from alcohol, yellow plates are obtained melting at 128°, and a nitrogen determination, made by Mr. A. P. Beardsley, gave the following result:

	Calculated for $C_{12}H_{13}O_3NS_2$.	Found.
N	4.94	5.00

When this urethane was treated with sodium alcoholate and ethyl chloracetate an oil was obtained. This boiled at 137° to 195° at 15 to 30 mm. pressure. A considerable portion distilling at 188° to 192° at 23 mm. pressure. This oil was free from nitrogen and agreed in properties with ethyl benzoylthioglycollate, $C_6H_5CO.SCH_2CO_2C_2H_5$, which, when pure, boils at 185° to 187° at 15 mm. pressure, and when mixed with aniline forms benzanilide.

Ethyl Acetate Derivative of Benzyl benzoylimidodithiocarbonate,



$$C_6H_5CO.N{=}C\begin{cases}SCH_2CO_2C_2H_5\\SCH_2C_6H_5\end{cases}$$

.—This was formed in a smooth manner when 8 grams of benzyl benzoyldithiocarbamate were dissolved in alcohol containing 0.64 gram of sodium and then 3.4 grams of ethyl chloracetate were added. On standing twelve hours water precipitated an oil, which easily solidified, and on crystallizing from strong alcohol colorless, flattened prisms, melting sharply at 79°, were obtained. Nitrogen and sulphur determinations gave the following results:

	Calculated for $C_{19}H_{19}O_3NS_2$.	Found.
N	3.75	3.63
S	17.15	17.04

Attempts to prepare this ester from the ethyl acetate derivative of benzoyldithiourethane and benzyl chloride, using sodium alcoholate in alcohol solution, were without success. A reaction soon took place and sodium chloride separated, but whether the ester was precipitated with water after an hour's standing, or longer, an oil was invariably obtained which showed no evidence of crystallizing after standing a number of weeks. It also refused to solidify in a freezing-mixture.

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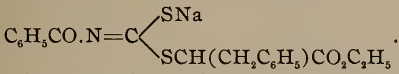
[1] Arch. der Pharm., 238, 9 (1900).

The α-Derivative of Ethyl Hydrocinnamate and Sodium Benzoyldithiocarbamic Acid,



$$C_6H_5CO.N{=}C\begin{cases}SNa\\SCH(CH_2C_6H_5)CO_2C_2H_5\end{cases}$$

.—When, instead of using alcoholic solutions, the ethyl acetate derivative of benzoyldithiocarbamic acid is shaken with benzyl chloride, in the presence of an excess of aqueous alkali, the oily turbidity which results at first gives place to a yellow solid. On crystallizing this from alcohol, in which it is quite difficultly soluble, granular, well-developed, transparent, bright-yellow prisms are obtained. This material has no definite melting-point but decomposes a little above 100° with effervescence and is generally completely melted at 175°. The results of the analysis of this compound are as follows :

	Calculated for $C_{19}H_{18}O_3NS_2Na$.	Found.	
C	57.72	....	
H	4.55	4.20	
N	3.54	3.62	
S	16.20	16.40	16.0
Na	5.82	5.93	

When this material is suspended in water, in which it is quite difficultly soluble, and carbon dioxide is passed into the solution,

The α-Derivative of Ethyl Hydrocinnamate and Benzoyldithiocarbamic Acid, $C_6H_5CONHCS.SCH(CH_2C_6H_5)CO_2C_2H_5$, is liberated. This crystallizes from alcohol in bunches of bright-yellow prisms, which melt sharply at 79°. In other words, it has the same melting-point as its isomer described above, but when the two are mixed the melting-point is lowered to 63°. *The compounds prepared in the two ways, in this case, are isomeric and not identical.* Attempts to convert the ethyl acetate derivative of benzyl benzoylimidodithiocarbonate into the above sodium salt had no effect on the material. Since the acylimidodithiocarbonic esters do not form salts, and since this compound has a bright yellow color, it is in all probability a dithiourethane as named above. The results of the analysis are as follows :

	Calculated for $C_{19}H_{19}O_3NS_2$.	Found.
C	61.12	60.79
H	5.09	4.70
N	3.75	4.05

Phenyl thiocyanacetate, $NCS.CH_2CO_2C_6H_5$.—Thirty grams of chloracetyl chloride and 26 grams of phenol, when heated on the water-bath, until hydrogen chloride was no longer evolved, gave 28.5 grams phenyl chloracetate boiling at 123° to 128° at 13 mm. pressure. This material reacted immediately with an alcoholic solution of potassium thiocyanate. The product was an oil which slowly solidified ; it was then crystallized from dilute alcohol, whereupon it was obtained in colorless plates which showed signs of melting at 28° and then melted completely at 31° to 32°. A nitrogen determination gave :

	Calculated for $C_9H_7O_2NS$.	Found.
N	7.25	7.19

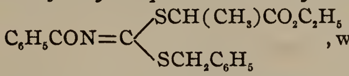
Phenyl Acetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CONHCS.SCH_2CO_2C_6H_5$.—When the above rhodanide was warmed in a little benzene with thiobenzoic acid and then, after a few hours, allowed to cool, a shining mass of bright-yellow needles separated, which on crystallizing from alcohol melted at 127° to 129°, and an analysis gave the following result :

	Calculated for $C_{16}H_{13}O_3NS_2$.	Found.
N	4.36	4.25

Experiments in alcoholic solutions with this compound and benzyl chloride, and with phenyl chloracetate on benzylbenzoyldithiocarbamate, as well as methyl benzoyldithiocarbamate and ethyl chloracetate, did not yield satisfactory products, since oils and tars were formed.

The α-Derivative of Ethyl Propionate and Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH(CH_3)CO_2C_2H_5$, when crystallized from alcohol and benzene, forms acicular yellow prisms which melt at 144° to 145°. The nitrogen determination is as follows:

	Calculated for $C_{13}H_{15}O_3NS_2$.	Found.
N	4.71	5.00

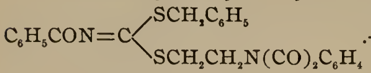
The α-Derivative of Ethyl Propionate and Benzylbenzoylimidodithiocarbonate,  $C_6H_5CON{=}C\begin{cases}SCH(CH_3)CO_2C_2H_5\\SCH_2C_6H_5\end{cases}$, was smoothly obtained in alcoholic solutions from benzyl benzoyldithiocarbamate and ethyl α-brompropionate. Prepared in this manner it forms colorless prisms, melting at 73° to 74°. The analytical results are as follows:

	Calculated for $C_{19}H_{20}O_3NS_2$.	Found.
C	62.01	61.09
H	5.42	5.58
N	3.61	3.67
S	16.53	16.83

When an attempt was made to prepare this compound from the α-derivative of ethyl propionate and benzoyldithiocarbamate and benzyl chloride, in alcoholic solution, a product was obtained, although in a less smooth manner than the above, which melted at 105° to 106°. After crystallizing from benzene and petroleum ether it formed stout, colorless prisms, which had a different appearance from the above. Whether the decided difference in melting-point of these two preparations is due to an impurity in one case, or to the fact that they are isomers, cannot be decided at present, since on repeating the preparation of the carbamate, from ethyl α-thiocyanpropionate in large quantities, a product of sufficient purity to convert into the imidoether was not obtained.

Phthalimidoethyl Benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2CH_2N(CO)_2C_6H_4$, forms fine, yellow needles, which are difficultly soluble in alcohol. When crystallized from chloroform it melted at 178° to 182°. It was converted directly into

Phthalimidoethyl Benzyl benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases}SCH_2C_6H_5\\SCH_2CH_2N(CO)_2C_6H_4\end{cases}$$

.–This resulted smoothly when benzyl chloride acted on the sodium ethylate solution of the above. When crystallized from alcohol it forms beautiful colorless needles melting at 119° to 120°. A nitrogen determination gave :

	Calculated for $C_{25}H_{20}O_3N_2S_2$.	Found.
N	6.08	6.36

Attempts to prepare this compound from benzyl benzoyldithiourethane and bromethylphthalimide were without success. At ordinary temperatures the bromide does not react ; when warmed in alcoholic solution, or when the urethane is treated with sodium and the bromide in benzene, decomposition occurs and benzyl rhodanide is formed.

Ethyl 1′-Thiocyanbenzene, $C_6H_5CH(SCN)CH_3$, from bromethylbenzene and potassium thiocyanate boiled for the most part at 157° to 159° at 36 mm. pressure. It formed a colorless oil which, on analysis, gave :

	Calculated for C_9H_9NS.	Found.
N	8.58	8.25

When this rhodanide was warmed with thiobenzoic acid no acyldithiourethane was formed. The product crystallized from alcohol in colorless prisms, melting constantly at 136° to 137°. It was insoluble in alkali, and a sulphur determination gave 17.74 per cent sulphur. The material was not further examined.

Desyl Thiocyanate, $C_6H_5COCH(SCN)C_6H_5$, results smoothly from bromdesoxybenzoin and alcoholic potassium thiocyanate. It crystallizes from alcohol in colorless prisms which melt at 110° to 111°. A nitrogen determination gave :

	Calculated for $C_{15}H_{11}ONS$.	Found.
N	5.53	5.55

An acyldithiourethane was not obtained when this rhodanide was heated in benzene solution with thiobenzoic acid.

The product was insoluble in alkali and crystallized from alcohol in colorless prisms which melted at 137°. A sulphur determination gave 18 per cent of sulphur. This compound was not further examined beyond establishing the fact that it is not desylthiolbenzoate, $C_6H_5CO.SCH(C_6H_5).COC_6H_5$ (melting-point 110° to 111°).

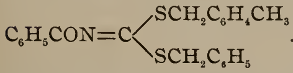
1′,m-Xylylthiocyanate $C_6H_4(CH_3)CH_2SCN$.—Metaxylyl bromide (boiling at 114° to 116° at 25 mm. pressure) readily reacts in alcoholic solution with potassium thiocyanate. The product is an oil which distils at 147° at 12 mm. pressure. It is colorless, has a disagreeable order and burning taste, but does not attack the eyes like the bromide. A nitrogen determination gave :

	Calculated for C_9H_9NS.	Found.
N	8.58	8.63

Metaxylyl Benzoyldithiocarbamate, $C_6H_5CO.NHCS.SCH_2C_6H_4CH_3$.—The above rhodanide and thiobenzoic acid readily combine when heated on the water-bath for several hours in benzene solution. The product is difficultly soluble in cold alcohol, readily in hot, from which it crystallizes in bright-yellow, needle-like prisms melting at 93° to 94°. A nitrogen determination gave :

	Calculated for $C_{16}H_{15}ONS_2$.	Found.
N	4.65	4.73

Benzylmetaxylyl Benzoylimidodithiocarbonate,



$$C_6H_5CON{=}C\begin{cases} SCH_2C_6H_4CH_3 \\ SCH_2C_6H_5 \end{cases}$$

.—When benzyl benzoyldithiocarbamate, sodium ethylate, and *m*-xylyl bromide were mixed in alcoholic solution, a reaction took place almost immediately, and the liquid became filled with a mass of bulky, colorless crystals. These were washed with water and crystallized three times from alcohol, whereupon they showed the constant melting-point of 97° to 98°. A nitrogen determination gave:

	Calculated for $C_{23}H_{21}ONS_2$.	Found.
N	3.58	3.69

On the other hand, when *m*-xylyl benzoyldithiocarbamate, sodium ethylate, and benzyl chloride were allowed to react, under precisely similar conditions to the above, the reaction took place much more slowly. When the two experiments were performed at the same time, the one above appeared to be complete before the latter separated any crystals. That the reaction was less smooth in this case was shown by the solution taking on a yellow color. After standing over night water precipitated a solid, which, after being crystallized six times from alcohol, melted for the most part at 85° to 86°, but did not become clear until 89°.5. It appeared that the melting-point of the material could not be altered by crystallizing from alcohol. A second experiment with carefully purified material gave the same result. Were it not for the fact that the material did not melt like a pure compound, it would be taken for an isomer of the ester melting at 97° to 98°.

In our next experiment, *m*-xylyl benzoyldithiocarbamate was dissolved in an excess of dilute aqueous sodium hydrate and shaken with benzyl chloride. A solid was thus obtained which after one or two crystallizations from alcohol melted sharply at 97° to 98°, and when mixed with the material of the same melting-point, prepared in the other way, the melting-point was not altered. The products proved to be identical in every respect. The fact was also established that this compound smoothly results when benzyl benzoyldithiocarbamate was treated in aqueous alkali with *m*-xylyl bromide.

Some attempts were made to determine exactly what impurity is present in the ester melting at 85° to 89°.5 by mixing various substances with the pure product melting at 97° to 98°. For example, the xylyl urethane, benzoyl disulphide, benzyl disulphide, benzylthiolbenzoate, etc. A product melting constantly at 85° to 89°.5, however, was not obtained.

Metaxylyl mercaptan, $CH_3C_6H_4CH_2SH$, forms a colorless oil with a disagreeable odor, which boils from 215° to 217° at ordinary pressures. A sulphur determination gave:

	Calculated for $C_8H_{10}S$.	Found.
S	23.18	22.88

This compound was converted into

Metaxylyl benzyl sulphide, $CH_3C_6H_4CH_2SCH_2C_6H_5$, which proved to be a colorless oil boiling at 193° to 196° at 15 mm. pressure. The product of the action of iodine on the alkaline solution of the above mercaptan (xylyl disulphide) was also obtained in the form of an oil. A sulphur determination in the case of metaxylyl benzyl sulphide gave:

	Calculated for $C_{15}H_{16}S$.	Found.
S	14.0	14.3

Dixylyl benzoylimidodithiocarbonic ester was smoothly formed in alcoholic solutions. It forms colorless prisms from alcohol which melt at 89°.5 to 90°. A nitrogen determination gave:

	Calculated for $C_{24}H_{23}ONS_2$.	Found.
N	3.45	3.51

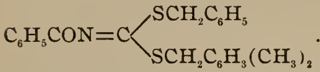
Mesityl thiocyanate, $(CH_3)_2C_6H_3CH_2SCN$, results smoothly from mesityl bromide and alcoholic potassium thiocyanate. It is very soluble in strong alcohol; from dilute, it forms beautiful colorless plates, which melt at 58°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}NS$.	Found.
N	7.90	7.78

Mesityl Benzoyldithiocarbamate,
$C_6H_5CONHCS.SCH_2C_6H_3(CH_3)_2$.—The crude product in this case was an oil, which was treated with sodium hydrate, and from the alkaline solution the urethane was precipitated by means of carbon dioxide. It crystallizes from alcohol in yellow plates or leaflets, which melt at 114°.5. A nitrogen determination gave:

	Calculated for $C_{17}H_{14}ONS_2$.	Found.
N	4.44	4.46

Benzyl mesityl benzoylimidodithiocarbonate,



$$C_6H_5CON=C\left\langle\begin{matrix}SCH_2C_6H_5\\SCH_2C_6H_3(CH_3)_2\end{matrix}\right.$$

.—The reaction in the case of benzyl benzoyldithiocarbamate, sodium ethylate, and mesityl bromide was practically complete in thirty minutes, and was perfectly smooth. This ester, on crystallizing from alcohol, formed prisms which melted at 117°.5. A nitrogen determination gave:

	Calculated for $C_{24}H_{23}ONS_2$.	Found.
N	3.23	3.25

When, under precisely similar conditions, mesityl benzoyldithiocarbamate (3 grams), sodium ethylate, and benzyl chloride were allowed to react, there was only a slight turbidity to indicate a reaction, after standing twelve hours. Water then precipitated an oil (small amount), and on passing carbon dioxide into the aqueous alkaline solution unaltered urethane (1.5 grams) was precipitated.

On the other hand, the imido ester results with the greatest ease, and in a few minutes, on simply shaking the aqueous alkaline solution of mesityl benzoyldithiocarbamate with benzyl chloride. The product had all the properties of the above ester melting at 117°.5.

From the results with xylyl and mesityl urethanes it might seem that aqueous solutions in general are more favorable than alcoholic for the preparation of acylimidodithiocarbonic esters, but this is not true, since it was found that ethyl chloracetate and ethyl α-brompropionate did not give imido esters with benzylbenzoyldithiourethane, while in alcoholic solution the esters are smoothly formed.

NEW HAVEN, CONN., April 22, 1901.

REVIEWS.

Chemical Lecture Experiments. By Francis Gano Benedict, Ph.D., Instructor in Chemistry in Wesleyan University. New York: The Macmillan Company; London: Macmillan & Co., L't'd. 1901. pp. 436 + xiii. Price, $2.00.

This is an attractive book that is likely to prove valuable to teachers of chemistry. The directions are clear, so that any one with proper training can follow them. The author says: "The object of this book is primarily to furnish teachers with a large number of reliable lecture experiments. That these experiments require in many cases different treatment from those performed in the laboratory will be obvious when it is considered that the demonstrations on a lecture-table must be of sufficient magnitude and of a character marked enough to enable the phenomenon to be observed at as great a distance as possible." * * * "All experiments requiring especially elaborate apparatus have here been rigorously excluded." * * * "The material here presented has been prepared with reference also to its use by students desiring collateral reading in connection with experimental lectures. As an elaboration of the laboratory manual the book may also be used by students for the preparation of many compounds not considered in elementary text-books."

A copy of the book should be available wherever chemistry is taught.

Laboratory Instructions in General Chemistry. Arranged by Ernest A. Congdon, Ph.B., F.C.S., Professor of Chemistry, Drexel Institute, Philadelphia. With 56 illustrations. Philadelphia: P. Blakiston's Son & Co. 1901. pp. 110. Price, $1.00.

This contains directions for laboratory work by students and, while it necessarily has much in common with other books prepared for the same purpose, it is distinguished by the evident care taken by the author in devising his experiments and in writing his directions. He says: "Much of the material is original, having been developed in the course of ten years' experience in laboratory teaching, while those portions taken from other sources have been modified and added to, so that they might better meet the wants of students."

Some of the experiments are rather difficult for a beginner, but that objection can be made to every course that has been prepared. With a good teacher and with plenty of time this course could be followed with profit.

An Elementary Treatise on Qualitative Chemical Analysis. By J. F. Sellers, A.M., Professor of Chemistry, Mercer University, Georgia. Boston: Ginn & Company. pp. v + 160.

This book is a new applicant for favor in a field already well occupied; but the work has distinctive merits. The author has consulted the latest and highest authorities on each topic; he has used good judgment in the selection of the matter of the book and in the quantity of matter introduced, thereby making the volume one of practical size and contents for the college student of qualitative analysis, who expects to proceed to quantitative work.

The methods of separation and proof are clearly stated, and they are generally those most approved by the best authorities. The author is careful fully to set forth the scientific principles on which processes depend; illustrative reactions are given wherever necessary; the teaching is so rationally and practically blended as to make dextrous and scientific workers.

More attention than usual in books of this size is devoted to the subjects of solution, osmosis, electrolytic dissociation, spectroscopy.

The book is full of valuable suggestions for the guidance of students in the care and use of apparatus, reagents, furniture.

R. W. Jones.

VOL. XXVI. SEPTEMBER, 1901. No. 3.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON THE OXYGEN ETHERS OF THE UREAS: METHYL- AND ETHYLISOUREA.[1]

BY RALPH H. MCKEE.

An investigation of the reactions of the isocarbanilides, $C_6H_5NH.C(:NC_6H_5)OR$, carried out by F. B. Dains,[2] under the direction of Professor Stieglitz,[3] in this laboratory, led to the discovery that these ethers show in some fundamentally important reactions—saponification and formation of amides—an entirely different behavior from the other known ethers with the same grouping $—C(:R'')OR—$, such as the ordinary acid esters $RC(:O)OR$ and the imido ethers $RC(:NH)OR$. The differences appear most striking on comparison of the isocarbanilides with the last-named closely-related class of bodies, the imido ethers, the two series of compounds having the group $—C(:NR)OR$ in common.

The hydrochlorides of the imidoethers, *e. g.*, of benzimidoether, etc., are rapidly saponified[4] in the cold in aqueous solution according to

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[1] See preliminary papers by J. Stieglitz and R. H. McKee: Ber. d. chem. Ges., **32**, 1494; **33**, 807 and 1517.

[2] J. Am. Chem. Soc., **21**, 136.

[3] This JOURNAL, **21**, 101.

[4] Quantitative determinations of the velocity of saponification of imidoethers by hydrochloric acid and water were carried out by Mr. Wm. McCracken, under my direction, in 1898 and 1899. They led to the highly interesting and important result

$$\text{(I)}\quad RC(:NH)OC_2H_5 + HCl + H_2O \longrightarrow RCOOC_2H_5 + NH_4Cl\,;$$

or

$$\text{(II)}\quad RC(:NH)OC_2H_5 + HCl + H_2O \longrightarrow RCONH_2 + C_2H_5OH + HCl.$$

The alkyl isocarbanilides, $RNH.C(:NR)OC_2H_5$, are much more stable in dilute acid solution, and when decomposed, for instance by prolonged heating with hydrochloric acid, even in the presence of a large excess of water (1 per cent acid) they invariably give carbanilides and alkyl chlorides according to

$$C_6H_5NH(:NC_6H_5)OC_2H_5 + HCl + H_2O \longrightarrow C_6H_5NHCONHC_6H_5 + ClC_2H_5 + H_2O.$$

Water apparently takes no part in the reaction.

The same contrast was shown in the behavior of the imidoethers and isourea ethers towards amines, such as anilines. Whereas imidoethers react easily, perhaps more readily than ordinary acid esters, and give amidines according to

$$RC(:NR)OC_2H_5 + C_6H_5NH_2 \longrightarrow RC(:NR)NHC_6H_5 + HOC_2H_5,$$

the isocarbanilides are scarcely acted on by aniline.[1]

This striking difference in reaction of bodies of the same class of compounds toward dilute hydrochloric acid, for instance, could well be due to the change from weaker bases (the imidoethers) to much stronger ones (the urea ethers), the change producing a corresponding difference in the hydrolysis of the hydrochlorides of the bases.[2] Such a result would have an important bearing on the question of the constitution of these hydrochlorides.[3] On account of this interesting connection, it was thought advisable to take into con-

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that addition of hydrochloric acid increases the velocity of saponification of an imidoether by water into ammonia and acid ester according to the above equation (I) up to a definite maximum velocity, produced by using 1 molecule of hydrochloric acid to 1 molecule of the free imidoether. Addition of more acid thereupon retards saponification (see this JOURNAL, **21**, 106). The experimental data and the discussion of the results obtained will be published later. Further work is being under taken on the velocity of saponification of imidoethers as well as on the velocity of the action of amines on imidoethers (see below). JULIUS STIEGLITZ.

[1] Dains : *Loc. cit.*

[2] Stieglitz : This JOURNAL, **21**, 105, etc.

[3] *Ibid.*, **21**, 102.

sideration, as an alternative possibility, another force that has been recognized as playing a pronounced rôle in the saponification and amide formation of acid esters. A loss or suppression of reactivity in the formation and saponification of acid esters[1] and acid amides[2] and in the formation of imidoethers[3] has in recent years been frequently found to be due to stereochemical interference of neighboring groups. Partly, in order to test the possibility of such interference as the cause of the surprising behavior of the isocarbanilides,

$$(PhNH)C(:NPh)OR,$$

and partly for the sake of completing the study of the preparation of isourea ethers. I have undertaken, at the suggestion and under the direction of Prof. Stieglitz, to prepare and examine isoureas of simpler structure than the isocarbanilides; *viz.*, first, the oxygen ethers of monoalphyl ureas, such as

$$(C_6H_5NH)(NH:)C.OR \text{ and } (C_6H_5NCH_3)(NH:)C.OR,$$

and secondly, the oxygen ethers of urea itself,

$$NH_2C(:NH)OR.$$

The methods developed for preparing these new classes of ethers will be described in the experimental part; they have made the ethers—including notably methyl and ethyl isourea,

$$NH_2C(:NH)OCH_3 \quad \text{and} \quad NH_2C(:NH)OC_2H_5,$$

as easily obtainable as any imidoether. It was found that these ethers can readily be benzoylated and condensed with phenyl isocyanate; thus were obtained isourea ethers with more negative groups, *e. g.*,

$$C_6H_5CONH.C(:NH)OR^4 \text{ and } C_6H_5CONHC(:NC_6H_5)OR,$$

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[1] V. Meyer and his pupils: Ber. d. chem. Ges., **27**, 510, 1580, 3146; **28**, 182, 1254, 2773, 3197; **29**, 830, 1397.

[2] Remsen: This Journal, **21**, 281, etc. Vide also, **1**, 32, 114, etc.

[3] Pinner: Ber. d. chem. Ges., **23**, 2917. [The question of interference with the saponification of imidoethers will be taken up with the velocity determinations.
J. Stieglitz.]

[4] Dixon (J. Chem. Soc. (London), 1899, 380) obtained the same substance by treating benzimidothiocarbonic esters, $C_6H_5CON:C(SR)OR$, with ammonia.

Vide also Wheeler and Johnson, this Journal, **24**, 189. The experiments described by me were all completed by last May (1900) before the appearance of Dr.

etc. Every isourea ether obtained gave an alkyl chloride and a urea on heating with even very dilute hydrochloric acid, *e. g.*, according to

$$NH_2C(:NH)OCH_3 + HCl + H_2O \longrightarrow NH_2CONH_2 + ClCH_3 + H_2O.$$

The study of the behavior of the new urea ethers towards amines has not been completed, but the question has been thoroughly investigated in the case of the monophenylated isoureas. In no instance was a smooth formation of an amide (guanidine)[1] observed, according to

$$C_6H_5NHC(:NH)OC_2H_5 + C_6H_5NH_2 \longrightarrow (C_6H_5NH)_2C:NH + C_2H_5OH.$$

The simple isourea ethers show, therefore, the same characteristic lack of power to form normal saponification-products and amides as the isocarbanilides; their characteristic behavior is, therefore, certainly not due to stereochemical interference of the groups attached to the nitrogen atoms and must, as was expected, be due to other causes.[2]

EXPERIMENTAL PART.

I. The Oxygen Ethers of the Monoalphylureas.

The oxygen ethers of the diphenylureas are prepared from the carbodiimides by the addition of alcohol according to

$$C_6H_5N:C:NC_6H_5 + HOR \longrightarrow (C_6H_5NH)C(:NC_6H_5)OR.$$

Wheeler's interesting paper (September number of this JOURNAL). Dr. Wheeler describes two or three of the bodies mentioned in the text, such as the ethyl and methyl benzoylphenylisoureas, which were obtained in approximately pure condition by means of Dixon's method. Dr. Wheeler also calls attention to the characteristic tendency of the isourea ethers to give alkyl chlorides with aqueous hydrochloric acid (Stieglitz : *Loc. cit.*; Dains : *Loc. cit.*; Stieglitz and McKee : Ber. d. chem. Ges., **33**, 1517), the acylated or more negative ones even reacting in that direction in the cold. In the case of one of these the solid hydrochloride was isolated by me and found to decompose spontaneously in the desiccator with evolution of alkyl chloride (p. 233). This behavior, it may be added, is entirely analogous to the behavior of the more negative imidoethers towards hydrogen chloride (*e. g.*, Stieglitz and Lengfeld : this JOURNAL, **16**, 75; **17**, 98; Ransom : *Ibid.*, **23**, 46).

[1] The actual reaction-products were interesting and will be described in the experimental part.

[2] The application of the results obtained to the theories suggested in this JOURNAL, **21**, 101, will be discussed by Prof. Stieglitz in a later paper after the collection of more data.

This addition may be accomplished by heating the diimide with absolute alcohol to 160° to 180° in sealed tubes,[1] or more simply in the cold by the action of sodium alcoholate[2] in alcohol solution on the carbodiimide, the reaction proceeding with great vigor and smoothness in the latter case.[3]

For the preparation of the monophenylisourea ethers the addition of alcohol to phenylcyanamide, $C_6H_5NH.CN$(I), or possibly $C_6H_5N : C : NH$(II)[4], was attempted on the lines mentioned; although in other addition reactions, *e. g.*, with hydrogen sulphide,[5] aniline,[6] etc., no great differences between the phenylcyanamides and the carbodiimides seem to have been noted,[7] it was found impossible to add alcohol to phenylcyanamide by the methods which had proved so successful with the carbodiimides. As such a behavior might be due to the presence of a nitril group in phenylcyanamide according to constitution (I), the compound was treated with alcohol (1 mol.) and hydrogen chloride (1 mol.) according to Pinner's method for converting a nitril into an imidoether. Only traces of a substance were obtained, which gave ethyl chloride when heated in a current of dry hydrogen chloride gas, in the way that imidoethers and isourea ethers do. However, it was soon found that by modifying the method and using a very large excess of alcohol, phenylcyanamide can be converted quantitatively into monophenylisourea ethers according to

$$C_6H_5NHCN + HOC_2H_5 + HCl \rightarrow C_6H_5NHC(:NH)OC_2H_5.HCl.$$

In this way methyl phenylisourea, ethyl phenylisourea, and ethyl-*o*-tolylisourea were prepared with ease in quantity.

The fact, on the one hand, that sodium alcoholate is taken up by carbodiphenylimide with great violence,[1] but not at all by phenylcyanamide, and the resemblance, on the other hand, in the method of adding alcohol to nitrils and to phenylcyanamide seemed strongly to favor, incidentally, the nitril constitution for phenylcyanamide, $C_6H_5NH.C \vdots N$, as against the carbodiimide constitution, $C_6H_5N:C:NH$.[2] How little such synthetic methods can be relied upon for distinguishing between tautomeric formulæ, without exhaustive study, is shown by the interesting fact that alkylphenylcyanamides,

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[1] Lengfeld and Stieglitz : Ber. d. chem. Ges., **27**, 926.

[2] Stieglitz : *Ibid.*, **28**, 573.

[3] A third method (Lengfeld and Stieglitz : This JOURNAL, **17**, 112), which consists in treating the diimide successively with dry hydrogen chloride and sodium alcoholate, is probably identical in the final character of the reaction with the second method given above.

[4] Meyer and Jacobson : Vol. II, 197.

[5] Weith : Ber. d. chem. Ges., **7**, 1303 ; **9**, 819.

[6] Weith : *Ibid.*, **7**, 13 ; Cahours and Cloez : Ann. Chem. (Liebig), **90**, 93.

[7] We now have reason to suspect that carbodiphenylimide is really the more reactive of the two.

$$(RNC_6H_5).C \vdots N,$$

undoubted nitrils, were found to take up alcohol far more readily by means of sodium alcoholate than by treatment with alcohol and hydrogen chloride, addition in the latter case taking place much more slowly than with phenylcyanamide. Undoubted carbodiimides, therefore, *e. g.*, $C_6H_5N{=}C{=}NC_6H_5$, and unquestionable nitrils, *e. g.*, $C_6H_5NCH_3.C \vdots N$, resemble each other in taking up alcohol to form isourea ethers easily in the presence of sodium alcoholate—while phenylcyanamide, whose constitution must resemble one or the other, does not take up alcohol at all under these conditions, but does so in acid solution more rapidly than the others. The chief regularity observed in this question is that those compounds which form metal salts, such as phenylcyanamide, of which salts $M'(C_6H_5NCN)$ are known, and cyanamide, which gives salts, $M'_2(N_2C)$, are less readily acted on by sodium alcoholate and more easily by hydrochloric acid and alcohol. With fully substituted cyanamides and carbodiimides which do not form metallic salts, but do absorb hydrochloric acid easily, the conditions are reversed. The conclusion is inevitable that constitution plays no rôle in this reaction while electric conditions of the molecule do.

Ethyl Phenylisourea (*Ethyl Phenylimidocarbamate*), $NH_2.C(:NC_6H_5)OC_2H_5$ or $NH:C(NHC_6H_5)OC_2H_5$.[3]—The addition of alcohol to phenylcyanamide was first attempted, as explained above, by the methods which had proved successful with the carbodiimides. As the negative result of the experiment is of some interest, the conditions observed will be very briefly given.

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[1] Stieglitz: *Loc. cit.*

[2] See preliminary reports, *Loc. cit.*

[3] The two formulæ represent the two tautomeric constitutions for the urea ether. As in the case of other amidines (Von Pechmann: Ber. d. chem. Ges., **28**, 2362 and 869; **30**, 1779. Wheeler: This JOURNAL, **19**, 367; **20**, 481 and 853; Marckwald: Ann. Chem. (Liebig), **286**, 348) only one form appears to be stable. The determination of

An alcoholic solution of crystallized phenylcyanamide,[1] $C_6H_5NH.CN + \frac{1}{2}H_2O$, was added to a cold solution of sodium ethylate, prepared by dissolving slightly more than one equivalent of sodium in absolute alcohol, and the whole was allowed to stand a day and a half. On pouring the mixture into water and neutralizing with acetic acid, the phenylcyanamide was recovered unchanged. Heating the mixture on the water-bath gave no better result.

Equivalent amounts of crystallized phenylcyanamide and absolute alcohol were heated in a sealed tube to 180°–200° for three and a half hours. On treating the contents of the tube with water no basic oil separated, thus showing that the phenylisourea ether had not been formed.

The method of preparation finally used was as follows: Three to 3.6 grams (1.5 to 2 mol.) dry hydrogen chloride were passed into a well cooled solution of 6.3 grams (1 mol.) crystallized phenylcyanamide in 18 to 23 grams (8 to 10 mol.) absolute ethyl alcohol. After standing two days the mixture was slowly poured into an excess of a cold 15 per cent solution of potassium hydroxide. The oil separating was taken up with ether and the extract washed several times with small amounts of water and dried with anhydrous sodium sulphate. After filtering from the sodium sulphate, by means of a siphon filter, the ether was distilled off on the water-bath and the oil remaining fractioned *in vacuo*. The second distillation gave fractions boiling at 138° to 138°.5, 138°.5, and 138°.5 to 139°.5 at 18 mm. pressure, the middle fraction being three-fourths of the entire amount. The yield of pure oil was 77.5 per cent of the theory.

the actual constitution by distinguishing between the two forms was not attempted, because the methods used in the case of other amidines did not seem at all conclusive. To avoid needless occupation of space only one formula will be used hereafter in such cases, it being understood that the tautomeric form is considered equally justified.

[1] Hofmann: Ber. d. chem. Ges., 18, 3220.

Ethyl phenylisourea is a colorless liquid having a basic amine-like odor. It is readily soluble in all the ordinary organic solvents, and slightly soluble in water, the solution resulting being strongly alkaline.

The ether boils at the following temperatures:

	Temperature.
12 mm.	131°
18 mm.	138°.5
32 mm.	155°

It could not be solidified by cooling to —15°. The index of refraction as determined with an Abbé refractometer is 1.5575 at 23°. Analysis:

I. 0.1642 gram substance gave 0.3971 gram CO_2 and 0.1152 gram H_2O.

II. 0.2861 gram substance gave 0.6913 gram CO_2 and 0.1937 gram H_2O.

	Calculated for $C_9H_{12}N_2O$.	Found. I.	II.
C	65.77	65.96	65.90
H	7.38	7.86	7.59

Dry hydrogen chloride was passed over a little of the oil contained in a test-tube connected with an azotometer. The hydrogen chloride was at first absorbed; on heating the tube in the water-bath to about 78° decomposition occurred, a gas (ethyl chloride) being evolved, which was not absorbed by a solution of caustic potash and which burned with a green flame. The solid in the tube, after crystallization from hot water, melted at 145°, and mixed with synthetic monophenylurea[1] (melting-point 147°) it melted half a degree higher. The decomposition takes place, therefore, according to

$$C_6H_5NHC(:NH)OC_2H_5 + HCl \rightarrow C_2H_5Cl + C_6H_5NHCONH_2,$$

confirming the constitution given to the isourea ether.

Ethyl Phenylisourea Hydrochloride, $C_6H_5NHC(:NH)OC_2H_5.HCl$.—A solution of ethyl phenylisourea in absolute ether, treated with dry hydrogen chloride, gave an immediate white crystalline precipitate of the hydrochloride. This was rapidly filtered off, well washed with absolute ether, and dried on a clay plate *in vacuo* over solid caustic potash and sulphuric acid. It was afterward finely powdered and replaced in the vacuum desiccator.

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[1] Weith: Ber. d. chem. Ges., 9, 820.

0.2883 gram substance required 14.35 cc. tenth-normal $AgNO_3$ (using chromate as an indicator).

	Calculated for $C_9H_{13}N_2OCl$.	Found.
Cl	17.67	17.65

The analysis shows that, while the phenylisourea contains both an anilide and an imide group, yet it is a monacid base towards hydrochloric acid, as far as the formation of a stable salt is concerned. The same result was obtained (see below) with hydrochlorplatinic acid. The water solution of the hydrochloride does not change the tint of neutral litmus paper, the solution being *exactly neutral* so far as could be determined by the use of litmus and of methyl orange as indicators.

If the ether solution is saturated with hydrogen chloride, a salt is obtained whose solution in water is acid to litmus and which contains a higher percentage of chlorine. One sample made contained 18.73 per cent, but on standing in the desiccator several days the percentage of chlorine became less, although it did not become quite as low as that of the pure monohydrochloride.

Ethyl phenylisourea hydrochloride is a white crystalline solid soluble in water, methyl and ethyl alcohols, chloroform, and acetone; insoluble in benzene, ligroin, and ether. Heated in a melting-point tube the salt melts at 110° with evolution of ethyl chloride. Once having been freed from excess of hydrogen chloride the salt is quite stable, seemingly being entirely unaffected by exposure to the air. Its stability towards water was shown by the fact that it could be crystallized from its concentrated water solution, forming beautiful clusters of needles an inch in length radiating from a common center.

Chlorplatinate of Ethyl Phenylisourea, $(C_9H_{12}N_2O)_2,H_2PtCl_6$. —On mixing somewhat concentrated absolute alcohol solutions of ethyl phenylisourea and chlorplatinic acid, the chlorplatinate slowly separated in the form of dark-yellow plates.

It was filtered off, washed with absolute ether, and dried on a clay plate *in vacuo* over sulphuric acid. It melts with decomposition at 160°, is insoluble in water, and difficultly soluble in alcohol.

Analysis:

0.1392 gram substance gave 0.0369 gram platinum.

	Calculated for $C_{18}H_{26}N_4O_2PtCl_6$.	Found.
Pt	26.40	26.51

Action of Air and Water on Ethyl Phenylisourea.

Imidoethers,[1] on exposure to the air or in contact with water, slowly give an acid amide and alcohol according to

$$RC(:NH)OR' + H_2O \longrightarrow RCONH_2 + R'OH.$$

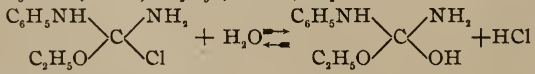
Under similar treatment the isourea ethers are very stable. Ethyl phenylisourea exposed to the air apparently undergoes no change. Neither did contact with water for six months nor heating with water for six hours at 100° produce a perceptible change. However, when the time of heating with water in a sealed tube was lengthened to fifteen hours there was some separation of monophenylurea. No ammonia or aniline could be found, making it certain that no urethane had been formed.

Dains[2] found that water does not act on ethyl diphenylisourea at ordinary temperatures.

Action of Dilute Hydrochloric Acid on Ethyl Phenylisourea.

The interest attaching to the products of the action of dilute hydrochloric acid on isourea ethers is explained in the introduction. If hydrolysis or saponification occurs as in the case of the imidoethers, ethyl phenylisourea would react as follows:[3]

I. $C_6H_5NHC(:NH)OC_2H_5 + HCl + H_2O \longrightarrow$



$$\begin{matrix}C_6H_5NH\\C_2H_5O\end{matrix}\!>\!C\!<\!\begin{matrix}NH_2\\Cl\end{matrix} + H_2O \rightleftarrows \begin{matrix}C_6H_5NH\\C_2H_5O\end{matrix}\!>\!C\!<\!\begin{matrix}NH_2\\OH\end{matrix} + HCl$$

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[1] Wheeler: This Journal, **17**, 398.

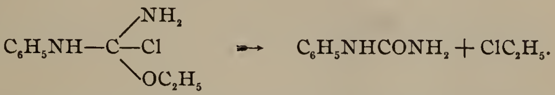
[2] J. Am. Chem. Soc., **21**, 166.

[3] Stieglitz: *Loc. cit.*; Dains: *Loc. cit.*

and would give either ammonia (or aniline) and a urethane or alcohol and phenylurea according to

$$\begin{aligned} &a.\ NH_3 + C_6H_5NHCOOC_2H_5\,; \\ \text{or } &b.\ C_6H_5NH_2 + NH_2COOC_2H_5\,; \\ \text{or } &c.\ C_2H_5OH + C_6H_5NHCONH_2. \end{aligned}$$

On the other hand it could give, without hydrolysis, as in the case of the isocarbanilides, ethyl chloride and phenylurea according to

II. 

$$C_6H_5NH-\overset{NH_2}{\underset{OC_2H_5}{C}}-Cl \longrightarrow C_6H_5NHCONH_2 + ClC_2H_5.$$

The following experiments show that ethyl phenylisourea is uncommonly stable towards aqueous hydrochloric acid at ordinary temperatures and is decomposed by it at 100° according to II and not according to I—in a word, as was expected, without hydrolysis of the urea ether salt.

Ethyl phenylisourea (1 mol.) with 8 per cent hydrochloric acid (1.1 mol.) was heated to boiling for two minutes, cooled, and kept at the room temperature. After two months the solution was still perfectly clear and a drop of alkali precipitated the unchanged urea ether.

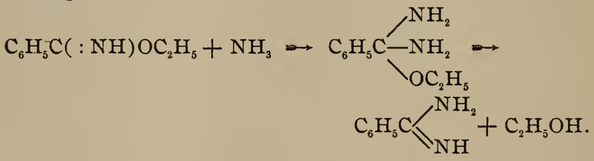
No change could be detected after heating the urea ether at 50°, for three and a half hours, with normal hydrochloric acid.

A solution of 1.7 grams ethyl phenylisourea in slightly more than 1 molecule 8 per cent hydrochloric acid was heated four and a half hours in a sealed tube in a Victor Meyer water-bath. The tube opened with considerable pressure, due to ethyl chloride, as the gas burned with the characteristic green flame. A deposit of crystals was separated from the mother-liquor (*a*) and then, to test them for any admixture of phenylurethane, distilled with steam, but no trace of the urethane could be found in the distillate. A single recrystallization of the residue gave pure monophenylurea. The clear filtrate (*a*) gave, with sodium hydroxide, an emulsion which was extracted with ether. Careful evaporation of the ether left a few drops of an oil, which was shown to contain a little aniline by the bleaching-powder test and unchanged isourea ether by the formation of ethyl chloride when heated in a current of dry hydrogen chloride. That the small amount of aniline found was most likely due to saponification of some of the phenylurea by the dilute acid was proved by heating monophenylurea (1 mol.) with dilute acid ($\frac{2}{3}$ mol.) for two hours, and showing the presence of aniline in the filtrate in approximately the same amount as found before.

The chief products of the action of hydrochloric acid on ethyl phenylisourea are, therefore, ethyl chloride and phenyl urea according to equation II.

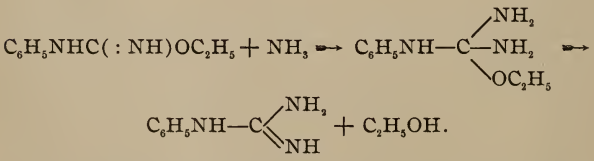
Action of Ammonia on Ethyl Phenylisourea.

In the introduction attention was called to the striking contrast in the behavior of isocarbanilide ethers and imidoethers towards amines. Thus ammonia readily reacts with benzimido ether with formation of benzamidine and alcohol[1] according to



$$C_6H_5C(:NH)OC_2H_5 + NH_3 \rightarrow C_6H_5C\begin{array}{l}\diagup NH_2\\ -NH_2\\ \diagdown OC_2H_5\end{array} \rightarrow C_6H_5C\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{array} + C_2H_5OH.$$

If a similar action occurred with the isourea ethers, ethyl phenylisourea should give monophenylguanidine and alcohol according to



$$C_6H_5NHC(:NH)OC_2H_5 + NH_3 \rightarrow C_6H_5NH-C\begin{array}{l}\diagup NH_2\\ -NH_2\\ \diagdown OC_2H_5\end{array} \rightarrow C_6H_5NH-C\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{array} + C_2H_5OH.$$

The experiments show that no action of this nature occurs, the urea ether being entirely unaffected by ammonia.

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[1] Stieglitz: *Loc. cit.*

Ethyl phenylisourea, after having been in contact with concentrated aqueous ammonia for two months at the room temperature, was recovered unchanged.

No action could be detected after heating the urea ether in a sealed tube with alcoholic ammonia for three hours at 140°, the urea ether being again entirely recovered.

If ammonia reacted with ethyl phenylisourea according to the above equation, monophenylguanidine would be one of the products. Feuerlein[1] has described a substance as monophenylguanidine, but the properties given are not those one would expect a guanidine to have.[2] For fear from lack of exact knowledge concerning its properties of overlooking the base if it had been formed only in small quantity, it seemed best to prepare the guanidine synthetically. Even after becoming familiar with its properties none could be found when phenylisourea was treated with ammonia.

Monophenylguanidine, $C_6H_5NHC(:NH)NH_2$.—Equivalent amounts of cyanamide and aniline hydrochloride were placed in a sealed tube with double the weight of absolute alcohol and heated at 100° for two and a half hours. The tube opened with no pressure. Its contents were evaporated on the water-bath nearly to dryness and redissolved in a little water. Addition of a concentrated solution of potassium hydroxide caused the guanidine to separate as an oil, which soon solidified and was then filtered off. The yield was excellent.

Monophenylguanidine is soluble in water, alcohol, ether, warm chloroform, and warm benzene. Crystallized from the last solvent it melted at about 66°.[3] It decomposes on attempting to distil it *in vacuo*. The free base is hygroscopic and takes up carbon dioxide; for identification the chlorplatinate and benzoyl derivatives were prepared and analyzed.

Monophenylguanidine Chlorplatinate,[4] $(C_7H_9N_3)_2H_2PtCl_6$.—Alcoholic solutions of monophenylguanidine and chlorplatinic acid were mixed, the resulting precipitate filtered off, washed with a little alcohol and ether, and dried *in vacuo*. The chlorplatinate is soluble in water and warm alcohol; it melts with decomposition at 197° to 198°.

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[1] Ber. d. chem. Ges., 12, 1602.

[2] Judging from the properties Feuerlein gives, the body he had was possibly the ammonium salt of phenylcyanamide.

[3] Feuerlein could not have had monophenylguanidine, for he describes the body as exploding when heated.

[4] Feuerlein states that monophenylguanidine does not form a chlorplatinate.

0.2693 gram substance gave 0.0774 gram platinum.

0.1256 gram substance gave 13.9 cc. moist nitrogen at 19° and 745.8 mm.

	Calculated for $C_{14}H_{20}N_6PtCl_6$.	Found.
Pt	28.65	28.74
N	12.39	12.53

Dibenzoylphenylguanidine, $C_6H_5CONH.C(:NCOC_6H_5).NHC_6H_5$. — When monophenylguanidine was treated with the equivalent amount of benzoyl chloride there was formed a small amount of a solid which proved to be not the mono- but the dibenzoyl derivative. This dibenzoyl derivative was formed quantitatively when monophenylguanidine (1 mol.) was dissolved in dilute caustic potash, benzoyl chloride (2 mol.) added, and the whole shaken until all odor of the acid chloride had disappeared. The resulting solid, when recrystallized from boiling alcohol, in which it was only slightly soluble, gave needles melting at 183°.5.

I. 0.1945 gram substance gave 0.5206 gram CO_2 and 0.0903 gram H_2O.

II. 0.1630 gram substance gave 18 cc. moist nitrogen at 24° and 745.4 mm.

	Calculated for $C_{21}H_{17}N_3O_2$.	Found. I.	Found. II.
C	73.41	73.00	....
H	5.00	5.20	....
N	12.27	....	12.21

While the free monophenylguanidine has hitherto been unknown the chloraurate[1] and picrate[2] have been described. Emick describes the gold salt as forming yellow-brown needles soluble in hot water. I found the needles to be of a light-yellow color after recrystallization from hot water. Prelinger describes the picrate obtained from Emick's chloraurate as forming dark-yellow needles melting at 208° to 214.° I found the needles to melt at 221°.

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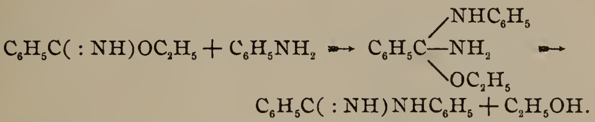
[1] Emick: Monatsh. Chem., **12**, 17.

[2] Prelinger: *Ibid.*, **13**, 100.

Action of Aniline on Ethyl Phenylisourea.

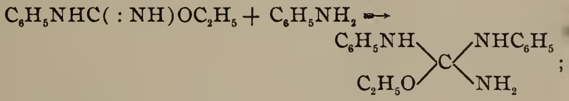
Imidoethers react smoothly with aniline, presumably first forming an addition-product from which, by the loss of alcohol, amidines result.



$$C_6H_5C(:NH)OC_2H_5 + C_6H_5NH_2 \rightarrow C_6H_5C\left\langle\begin{matrix}NHC_6H_5\\NH_2\\OC_2H_5\end{matrix}\right. \rightarrow C_6H_5C(:NH)NHC_6H_5 + C_2H_5OH.$$

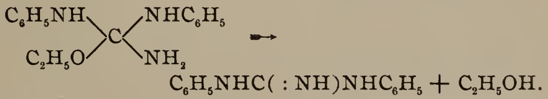
With ethyl phenylisourea a similar addition of aniline and splitting off of alcohol with formation of diphenylguanidine might take place as follows:

I.



$$C_6H_5NHC(:NH)OC_2H_5 + C_6H_5NH_2 \rightarrow \begin{matrix}C_6H_5NH\\C_2H_5O\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NHC_6H_5\\NH_2\end{matrix};$$

II*a*.



$$\begin{matrix}C_6H_5NH\\C_2H_5O\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NHC_6H_5\\NH_2\end{matrix} \rightarrow C_6H_5NHC(:NH)NHC_6H_5 + C_2H_5OH.$$

Experiment showed, however, that *no* guanidine results from the action of aniline on ethyl phenylisourea. This result is the more surprising as the actual products of the reaction point to the formation of the very reaction-product I. which, it would be supposed, would easily yield the guanidine. The most prominent reaction-products proved to be monoethylaniline and ethylamine, monophenylurea and diphenylurea. The formation of these four substances may be simply explained by assuming them to be decomposition-products of the addition-product I.:

II*b*. $C_6H_5NHC_2H_5 + C_6H_5NHCONH_2$;

II*c*. $C_2H_5NH_2 + C_6H_5NHCONHC_6H_5$.

But if that is the case, the absence of any tendency to form the guanidines is most surprising. In point of fact, the power of the urea ether to *alkylate* amines is worthy of note. No evidence of the occurrence of the fourth possible reaction,

$$\text{II}d.\ NH_3 + C_6H_5NHC(:NC_6H_5)OC_2H_5,$$

the formation of ammonia and ethyl isocarbanilide could be detected. The following is the experimental work on which the above statements are based:

Aniline and ethyl phenylisourea were heated for several hours at 150° without reacting. When molecular proportions of aniline and the phenylisourea were heated together for four hours at 175° a partial reaction occurred.

The tube opened with slight pressure, due to ethylamine, as was shown by passing the gas into dilute hydrochloric acid. On treating the residue left on evaporating the acid solution with chloroform and caustic potash, a strong isonitril odor was obtained. The contents of the tube were treated with cold dilute hydrochloric acid, filtered from a small amount of tar, and the filtrate (A) brought to boiling, but no precipitate separated, showing the absence of any ethyl isocarbanilide, which, if present, would have given a precipitate of carbanilide.[1] The tar, when extracted with boiling water, gave crystals of monophenylurea, identified by the melting-point (when mixed with the synthetic monophenylurea the melting-point was unchanged). The tarry mass which had been extracted with hot water was dissolved in hot alcohol, but the product which separated on cooling, while probably carbanilide, could not be positively identified owing to its small amount and to the simultaneous separation of the tar. In another experiment,[2] where the experiments were but slightly changed, carbanilide was completely identified. The dilute acid solution (A) was made alkaline and distilled with steam; in the distillate, besides much aniline (bleaching-powder test), the presence of ethylaniline and ethylphenylisourea was shown as follows: Ethylaniline was identified by acidifying a portion of the distillate, adding a little sodium nitrite and obtaining the yellow solution of nitrosoethylaniline. For confirmation, parallel experiments were carried out with a solution of aniline and the isourea ether, and with a solution of aniline, isourea ether, and a little ethylaniline; only the latter gave the yellow-colored solution expected. That unchanged ethyl phenylisourea was present was made certain by heating a few drops of the oil from the distillate in a current of hydrogen chloride and obtaining ethyl chloride. The residue left in the flask, after distilling with steam, was made acid, evaporated to a small volume, filtered, and the filtrate made alkaline with potassium hydroxide, but no guanidine separated.

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[1] Lengfeld and Stieglitz: *Loc. cit.*

[2] Page 225.

If the interpretation that has been given of the action of aniline on ethylphenylisourea is correct, the presence of a small amount of acid would accelerate the reaction, serving as it would to bring the double bond between the carbon and nitrogen atoms into the nascent condition,[1] and conversely a large excess of acid would retard, if not entirely stop, the reaction. Experiments fully confirmed these conclusions.

Molecular proportions of phenylisourea and aniline, with 1 molecule of hydrochloric acid, reacted at 50° in three hours, giving ethylaniline, ethylamine, monophenylurea, and carbanilide.

When aniline and ethyl phenylisourea were heated under the same conditions, excepting that four times as much acid was present, no action took place.

Action of Benzoyl Chloride on Ethyl Phenylisourea.

Dains[2] found that acyl chlorides acted upon ethyl isocarbanilide with the formation of ethyl chloride and a trisubstituted urea according to

$$C_6H_5NHC(:NC_6H_5)OC_2H_5 + R.COCl \rightarrow C_6H_5NH.CO.N(.COR)C_6H_5 + C_2H_5Cl.$$

This action of acyl chlorides corresponds in every way to that found by Wheeler and Walden[1] to occur when imidoesters having no hydrogen directly bound to the nitrogen atom are acted upon by acyl chlorides.

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[1] If the constitution of the urea ether salts is $(RNH)(NH_2)CCl(OR)$, the presence of insufficient acid to neutralize all of the base would tend to make the molecules change continually from the saturated salt condition to the unsaturated base $RNHC(:NH)OR$ and back again. Excess of acid would form the stable saturated salt. (Vide Stieglitz: "On the Constitution of the Salts of Carbimido Derivatives," *Loc. cit.*, p. 109).

[2] J. Am. Chem. Soc., **21**, 181.

I found that the monophenylated urea ethers can be benzoylated quite readily without the loss of the alkyl group, the reaction proceeding along the same lines as with the imidoethers, which have a replaceable hydrogen atom in the imido group. The benzoyl compounds in the urea series are much more stable towards moisture, ammonia, aniline, etc., than the benzoyl imidoethers. Towards heat the stability is reversed, it being found impossible to distil the benzoylated urea ethers without decomposition,[2] a property which rendered their purification difficult. This difficulty was in good part overcome by taking every care in the preparation to obtain a pure compound. A compound such as ethyl phenylisourea could produce two isomeric benzoyl derivatives, *viz.*,

$$C_6H_5NH.C(:NCOC_6H_5)OC_2H_5$$

and $$C_6H_5CO(C_6H_5)N.C(:NH)OC_2H_5.$$

As a matter of fact, a mixture of the two benzoyl derivatives is formed, for, when the resulting product is heated with hydrochloric acid a small amount of benzanilide, having the phenyl and benzoyl groups linked to the same nitrogen atom, is found as well as a larger amount of symmetrical benzoylphenylurea, in which the groups are bound to different nitrogen atoms. In the case of the benzoylated ethyl ether of phenylisourea it has not been found possible as yet to separate the isomers, but the separation was accomplished in the corresponding methyl series, and the compounds in question will be described more completely below. Working in the cold, the chief product is the symmetrical ether,

$$C_6H_5NH.C(:NCOC_6H_5)OC_2H_5.$$

Ethyl phenylisourea (2 mol.) was dissolved in five times the volume of absolute ether, and to this solution, kept in a freezing-mixture, there was slowly added, by means of a dropping funnel, a solution of benzoyl chloride (1.05 mol.) in four times the volume of absolute ether. In order to complete the reaction, the corked flask was allowed to stand an hour and a half in the freezing-mixture, and then, after reaching the room temperature, the ether solution was filtered by means of a siphon filter, from the solid precipitate of ethyl phenylisourea hydrochloride. Evaporation of the ether filtrate in a vacuum desiccator over sulphuric acid and caustic potash gave an oil mixed with a little solid. The former was taken up with ligroin (boiling-point 40° to 60°) and filtered from the undissolved solid, which consisted principally of the hydrochloride of ethyl phenylisourea. Sometimes there was formed at this point a small amount of a solid slightly soluble in ligroin and insoluble in water, the mass of which was greater if the operation was hurried and the temperature not kept low. The ligroin solution, on evaporation *in vacuo* over sulphuric acid, caustic potash, and paraffin, left the ethyl phenylbenzoylisourea as a nearly clear oil. On attempting to distil the oil at a pressure of 9 mm. it decomposed when the metal-bath reached 200°; on opening the flask the strong odor of phenyl isocyanate was present, and after that had disappeared an odor like that of benzonitril remained. The uninviting tar remaining in the flask was not investigated.

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[1] This JOURNAL, 19, 130.

[2] This has since been confirmed by Wheeler's experience. See this JOURNAL, 24, 219.

An analysis of the carefully prepared oil was made without distillation or farther purification and gave the following figures:

0.1401 gram substance gave 13.0 cc. moist nitrogen at 24° and 754.8 mm. pressure.

	Calculated for $C_{16}H_{16}N_2O_2$.	Found.
N	10.47	10.39

The product is therefore nearly pure ethyl benzoylphenylisourea. The oil consists chiefly of the symmetrical compound ethyl phenylimidobenzoylcarbamate,[1]

$$C_6H_5CO.N : C(NHC_6H_5)OC_2H_5,$$

with the benzoyl group attached to the non-phenylated ammonia rest. This is shown by the fact that treatment with dry hydrogen chloride decomposes it into ethyl chloride and symmetrical benzoylphenylurea, $C_6H_5CONHCONHC_6H_5$, (melting-point 203°.5 to 204°, not changed by mixing with the synthetically[1] prepared compound). At the same time the benzoylated urea ether probably contains a small amount of the isomeric compound with the benzoyl group attached to the aniline radical, ethyl imidobenzoylphenylcarbamate,

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[1] See Wheeler: This JOURNAL, 24, 219.

$$C_6H_5CO(NC_6H_5)C(:NH)OC_2H_5.$$

After standing for some months in a desiccator the oil deposited a quantity of slender prisms, which resembled in habit the corresponding solid asymmetric benzoyl derivative of methyl phenylisourea (see below). The difference in solubility of the oil and solid in low-boiling ligroin did not admit of their separation as in the methyl series.

Action of Dilute Hydrochloric Acid on Ethyl Benzoylphenylisourea.

The oily mixture of the two isomeric ethyl benzoylphenylisoureas was heated for three and a half hours at 100° with slightly more than the equivalent amount of normal hydrochloric acid. The tube opened with pressure due to ethyl chloride, which burned with its characteristic green-tinged flame. The solid was filtered off and by fractional crystallization from alcohol separated into benzoylphenylurea (melting-point 203°, unchanged when mixed with the synthetic product[2]) and about a fourth as much benzanilide (melting-point 160° to 161°, unchanged when mixed with the synthetic product). From the relative amounts of the solids obtained one can roughly estimate the percentage of each isomer in the mixture.

No alcohol could be found in the filtrate by the iodoform test.

Methyl Phenylisourea (Methyl Phenylimidocarbamate), $NH:C(NHC_6H_5)OCH_3$, was prepared by treating 16 grams (1 mol.) of crystallized phenylcyanamide dissolved in 40 grams (10 mol.) of absolute methyl alcohol with 7.6 grams

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[1] Kuhn: Ber. d. chem. Ges., **17**, 2881.

[2] *Loc. cit.*

($1\frac{2}{3}$ mol.) of dry hydrogen chloride. After standing two days the solution was worked up by the same method that was used in the case of the ethyl ether.

Methyl phenylisourea boils at the following temperatures:

	Temperature.
10 mm.	124°
15 mm.	133°
23 mm.	140°

It solidifies readily, forming a beautiful crystalline body (melting-point 46°.5) having a basic fishy odor and a bitter taste. The yield varied between 75 and 85 per cent of the theory. A freshly distilled portion was used for analysis:

I. 0.2742 gram substance gave 0.6437 gram CO_2 (H_2O lost).

II. 0.1470 gram substance gave 24.6 cc. moist nitrogen at 21° and 744.6 mm.

	Calculated for $C_6H_5NHC(:NH)OCH_3$.	Found. I.	II.
C	63.92	64.02	....
H	6.73	lost	....
N	18.70	....	18.75

Methyl Phenylisourea Hydrochloride, $C_6H_5NHC(:NH)OCH_3.HCl$, was formed by treating the solution of the methyl compound in absolute ether with hydrogen chloride. Like the hydrochloride of the ethyl ether this body, unless filtered and washed rapidly, takes up moisture from the air, forming a smear. When once freed from the excess of hydrogen chloride and ether, however, it is stable in the air. The hydrochloride is soluble in water and the ordinary organic solvents except ether, ligroin, and benzene. Heated in a tube it melted at 90° with evolution of a gas, which burned at the mouth of the tube with a green flame, showing it to be methyl chloride. The tube and contents were allowed to cool, and on reheating the substance melted at 145° (pure monophenylurea melts at 147°). The following action occurs:

$$C_6H_5NHC(:NH)OCH_3.HCl \rightarrow CH_3Cl + C_6H_5NHCONH_2.$$

The aqueous solution of the hydrochloride is neutral to litmus.

0.1305 gram substance required 6.97 cc. tenth-normal $AgNO_3$ (chromate indicator).

	Calculated for $C_8H_{11}N_2OCl$.	Found.
Cl	18.99	18.93

Methyl Phenylisourea Sulphate, $(C_8H_{11}N_2O)_2SO_4$.—A weighed amount of the crystals of the free base was dissolved in the theoretical volume of normal sulphuric acid and the resulting neutral solution allowed to evaporate *in vacuo* over solid caustic potash and concentrated sulphuric acid. A very viscous amorphous mass was left, which, by continued scratching, finally became solid. When dissolved in warm acetone and allowed to cool the sulphate separated in crystalline plates which melted at about 139°.

An analysis was made by titrating with barium chloride, potassium bichromate, and ammonia.

0.1920 gram substance required 9.65 cc. tenth-normal $BaCl_2$.

	Calculated for $C_{16}H_{22}N_4O_6S$.	Found.
SO_4	24.11	24.14

Action of Dilute Hydrochloric Acid on Methyl Phenylisourea.

Methyl phenylisourea, when heated with 8 per cent hydrochloric acid (1.1 mol.) for four hours at 100°, gave much methyl chloride and monophenylurea (melting-point 147°). The reaction takes place according to

$$C_6H_5NHC(:NH)OCH_3 + H_2O + HCl \rightarrow CH_3Cl + C_6H_5NHCONH_2 + H_2O,$$

the water, although in large excess, taking no part in the reaction.

Action of Benzoyl Chloride on Methyl Phenylisourea.

Two and a half grams ($1\frac{1}{7}$ mol.) methyl phenylisourea were dissolved in ten times the volume of alcohol-free ether, 4 grams (2 mol.) of a 33 per cent caustic potash solution added, and to the whole, kept cold by ice-water, 2 grams (1 mol.) benzoyl chloride, dissolved in 7 grams ether, added. The flask was vigorously shaken for half an hour or until all the benzoyl chloride had been used up. The ether solution was washed once with water to get rid of the excess of alkali, once with very dilute hydrochloric acid to take out all unused methylphenyl isourea, and finally, after washing three more times with water, dried with anhydrous sodium sulphate. Evaporation of the ether solution left an oil mixed with a very little solid. The oil was at once taken up with 65 cc. dry ligroin (boiling-point 40° to 60°), and on evaporation of this ligroin solution *in vacuo* over paraffin and sulphuric acid to half its original volume, crystals (B) separated. The ligroin solution remaining was poured into a second beaker, and further evaporation left an oil mixed with some crystals. On redissolving the oil in ligroin and evaporating again a clear oil (A) was obtained. That the oil and crystals are isomeric benzoyl derivatives of methyl phenylisourea, the oil having the benzoyl and phenyl groups bound to different nitrogen atoms, and the solid having these groups attached to the same nitrogen atom will now be shown.

Symmetrical Methyl Benzoylphenylisourea,[1] $C_6H_5CONHC(:NC_6H_5)OCH_3$.—0.26 gram of the oil (A) heated in a current of dry hydrogen chloride began to evolve methyl chloride at about 35°. The urea left in the tube, after recrystallizing once from alcohol, melted at 203° to 204°; mixed with the synthetic[2] symmetrical benzoylphenylurea the melting-point was still 203° to 204°. The decomposition,

$$C_6H_5CONH.C(:NC_6H_5)OCH_3 + HCl \longrightarrow C_6H_5CONH.CO.NHC_6H_5 + CH_3Cl,$$

shows that the oil is the symmetrical methyl benzoylphenylisourea. Analysis of the oil gave the following figures:

0.1711 gram substance gave 16.0 cc. moist nitrogen at 17° and 751.8 mm.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.05	10.77

The interesting observation was made that the symmetrical methyl benzoylphenylisourea forms salts with bases as well as with acids. A little of the oil was dissolved in alcohol and water added until the solution had become quite turbid. Addition of a few drops of a solution of caustic potash (1 : 2) caused the turbidity to disappear.

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[1] Wheeler and Johnson: *Loc. cit.*

[2] Kuhn: Ber. d. chem. Ges., 17, 2881.

On adding a little acid to this clear solution it again became turbid, and now by adding either more acid or more alkali the turbidity could be caused to disappear. The silver salt can be formed by addition of silver nitrate to a solution of the potassium salt. The study of the constitution of these and analogous salts will be undertaken in the near future.

Asymmetrical Methyl Benzoylphenylisourea, $(C_6H_5CONC_6H_5)C(:NH)OCH_3$.—The solid isomer (B) was washed several times with ligroin (boiling-point 40° to 60°) and dried on a clay plate *in vacuo* over paraffin. It then melted at 64° to 65°.

0.1661 gram substance gave 15.7 cc. moist nitrogen at 16° and 750 mm.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.05	10.91

When treated the same as the isomeric oil (A) this compound also formed a potassium and a silver salt.

Asymmetrical Benzoylphenylurea, $C_6H_5CONC_6H_5.CO.NH_2$.—Some of this solid methyl benzoylphenylisourea heated in a current of dry hydrogen chloride evolved methyl chloride quantitatively according to

$$C_6H_5CONC_6H_5.C(:NH)OCH_3 + HCl \rightarrow CH_3Cl + C_6H_5CONC_6H_5.CO.NH_2.$$

The residue left in the tube after recrystallizing twice from alcohol melted at about 146°, but the liquid formed on melting was always cloudy, as if on melting there was decomposition. That the residue was not monophenylurea (melting-point 147°) was shown by the fact that a mixture of the two melted 20° lower. The unsymmetrical benzoylphenylurea not being known, the compound was identified by analysis :

I. 0.2170 gram substance gave 0.5570 gram CO_2. [H_2O lost.]

II. 0.1478 gram substance gave 15.6 cc. moist nitrogen at 16°.5 and 747.5 mm.

	Calculated for $C_{14}H_{12}N_2O_2$.	Found. I.	II.
C	69.94	70.00	....
H	5.05	lost	....
N	11.69	....	12.12

Symmetrical benzoylphenylurea melts 60° higher; *viz.*, at 204°.

Methyl (Sym) Diphenylisobiuret, $C_6H_5NH.C(OCH_3):NCONHC_6H_5$.—This compound is formed on mixing cold absolute ether solutions of methylphenylisourea and phenyl isocyanate[1] (slightly less than one equivalent), a solid separates and the precipitation is completed by the addition of low-boiling ligroin, in which the isobiuret is almost insoluble. After recrystallizing the compound by dissolving it in ether and again precipitating it with ligroin, its melting-point was found to be 111°. The substance is soluble in chloroform, alcohol, and ether.

0.1490 gram substance gave 20.5 cc. moist nitrogen at 17°.5 and 747.4 mm.

	Calculated for $C_{15}H_{15}N_3O_2$.	Found.
N	15.64	15.72

The isobiuret is formed according to

$$C_6H_5NHC(:NH)OCH_3 + C_6H_5NCO \longrightarrow C_6H_5NHC(OCH_3):NCONHC_6H_5.$$

Its structure was determined as follows: Dry hydrogen chloride passed into a solution of the substance in cold ether, to which a little alcohol had been added to increase the solubility of the base, gave a precipitate of the hydrochloride. On drying this salt *in vacuo* it lost methyl chloride spontaneously, giving a compound free from chlorine. A portion which had been dried over night in a vacuum desiccator, when recrystallized once from alcohol, gave a product melting at 209°.5 to 210°. Hofmann[1] describes α-diphenylbiuret,

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[1] Prepared according to the method of Dains: J. Am. Chem. Soc., **21**, 165 (Cf. Lengfeld and Stieglitz: This JOURNAL, **16**, 71; and Folin: *Ibid.*, **19**, 336).

$$(C_6H_5NH.CO)_2NH,$$

as melting at 210°. Decomposition was effected therefore according to

$$C_6H_5NH.C(.OCH_3):NCONHC_6H_5 + HCl \longrightarrow C_6H_5NHCONHCONHC_6H_5 + CH_3Cl.$$

Ethyl Tolylisourea (*Ethyl o-Tolylimidocarbamate*), $NH_2C(:NC_7H_7)OC_2H_5$.—The behavior of *o*-tolylcyanamide towards alcohol showed that the peculiarities of the conditions for adding alcohol to phenylcyanamide are characteristic of the group of alphylcyanamides and not restricted to the one cyanamide. Like phenylcyanamide, it did not respond to the treatment with alcohol and sodium ethylate, but was readily converted into the ether by treatment with a large excess of alcohol and a little hydrogen chloride.

o-Tolylcyanamide has previously been described by Voltmer,[2] who obtained it by the action of hydroxylamine on the mustard oil. It was prepared in quantity by desulphurizing *o*-tolylthiourea[3] with an alkaline solution of lead acetate according to the method used by Hofmann[4] with phenylthiourea. Its melting-point was found to agree with that given by Voltmer.

o-Tolylcyanamide (1 mol.) was treated with absolute alcohol (10 mol.) and hydrogen chloride (2 mol.). After standing two days the contents of the flask were worked up according to the same method of procedure that was applied to ethyl phenylisourea. For purification the crude oil was dissolved in ligroin (40° to 60°), filtered from a small mass of *o*-tolylurea crystals, the ligroin distilled off, and the oil fractioned twice *in vacuo*. The isourea boils at 144° (19 mm.). It could not be solidified. In its solubilities, taste, and odor it is very similar to the phenylisourea ethyl and methyl ethers.

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[1] Ber. d. chem. Ges., 4, 265.

[2] *Ibid.*, 24, 381.

[3] Prepared by heating together *o*-toluidine hydrochloride and ammonium sulphocyanide.

[4] Ber. d. chem. Ges., 18, 3220.

Analysis of the isourea ether gave the following figures:

0.2101 gram substance gave 29 cc. moist nitrogen at 21° and 749.5 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	15.57

On heating in a current of dry hydrogen chloride some of the oil contained in a tube connected with an azotometer, an evolution of gas took place as low as 56°. The gas was identified as ethyl chloride by its green-colored flame. The solid remaining in the tube after recrystallization from hot water melted at 190°. As this is a higher melting-point than the literature[1] gives for mono-*o*-tolylurea which should have been formed in the reaction, the urea was prepared from *o*-toluidine hydrochloride and potassium cyanate. Crystallized from hot water it melted at 190°; mixed with that obtained from the isourea ether the melting-point was not changed.

Ethyl o-Tolylisourea Chlorplatinate, $(C_{10}H_{15}N_2O)_2PtCl_6$.—On adding an excess of an alcoholic solution of chlorplatinic acid to a solution of the tolyl ether in absolute ether the orange-yellow chlorplatinate separates at once. Washed with absolute ether and dried *in vacuo* the crystals were found to melt with evolution of a gas at 177°. Under the microscope the crystal form is seen to be that of hexagonal prisms.

0.3895 gram substance gave 0.0986 gram platinum.

	Calculated for $C_{20}H_{30}N_4O_2PtCl_6$.	Found.
Pt	25.43	25.31

Action of Dilute Hydrochloric Acid on Ethyl o-Tolylisourea.

Ethyl tolylisourea showed the same behavior towards dilute hydrochloric acid as did the phenylisourea ethers. Heated with slightly more than the equivalent amount of 8 per cent hydrochloric acid for four hours at 100° it gave much ethyl chloride and *o*-tolylurea (melting-point 190°).

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[1] Voltmer: Ber. d. chem. Ges., **24**, 382, gives 189°; Beilstein's Handbuch (Cosack: Ber. d. chem. Ges., **13**, 1089) gives 185°.

Methylphenylcyanamide (*methyl cyanilide*),[1] $C_6H_5N(CH_3).CN$, was prepared in order to obtain and study unsymmetrically disubstituted isourea ethers, $R_2NC(:NH)OR$, and to see if an alkyl phenylcyanamide, an undoubted imido nitril, would conduct itself in the same way towards alkaline and acid alcohol solutions as phenylcyanamide (see p. 214).

Eight and three-tenths grams (1 mol.) of methyl phenylthiourea[2] were added to 35 cc. (4 mol.) of a hot solution of caustic potash (1 : 2) in which it only partially dissolved. To the mixture a hot concentrated solution of 23 grams (4 mol.) lead acetate was then added and the whole heated in the water-bath for a few minutes.

The beaker was cooled, its contents extracted several times with ether, and the ether solution dried with fused calcium chloride. On distilling off the ether in the water-bath, an amount of very nearly pure methylphenylcyanamide, corresponding to a yield of 82 per cent of the theory, was obtained. Distillation with steam gave it in beautiful colorless plates having a spicy nitril odor and melting at 30°.5.

Methylphenylcyanamide is readily soluble in all the ordinary organic solvents and in the concentrated mineral acids, but practically insoluble in dilute acids. It can be obtained pure by crystallization from a large volume of water or by distillation with steam.

0.2045 gram substance gave 0.5443 gram CO_2 and 0.1150 gram H_2O.

	Calculated for $C_6H_5NCH_3CN$.	Found.
C	72.64	72.59
H	6.11	6.30

Asymmetrical Ethyl Methylphenylisourea (*Ethyl Imidophenylmethylcarbamate*), $(C_6H_5NCH_3)C(:NH)OC_2H_5$.—In contrast with the behavior of phenylcyanamide towards sodium ethylate and alcohol its methyl derivative is most readily converted into the above ether by slowly adding a solution of 13.2 grams

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[1] This has since been prepared by Wallach (Ber. d. chem. Ges., **32**, 1872) from methylaniline and bromcyanogen, and by Traube and Wedelstädt (Ber. d. chem. Ges., **33**, 1384) by methylating phenylcyanamide in the presence of sodium alcoholate. Wallach describes it as melting at 28° and boiling at 136° (10 mm.).

[2] Gebhardt: Ber. d. chem. Ges., **17**, 2094.

(1 mol.) methylphenylcyanamide in 50 grams absolute alcohol in the cold to 32 grams absolute alcohol, in which 2.5 grams (1.1 atoms) sodium has been dissolved. Scarcely any rise of temperature is observed, while in a similar reaction between sodium alcoholate and carbodiphenylimide[1] very much heat is evolved. The mixture was allowed to stand two days and then carbon dioxide was run into it for fifteen minutes, the mass poured into 0.5 liter of water, and the whole extracted four times with ether. The farther treatment was the same as for the preparation of ethylphenylisourea (see above). Sixteen grams of the slightly colored crude isourea ether, *i. e.*, 90 per cent of the theoretical yield, was obtained. The boiling-point of the pure ether was found to be 137° (21 mm.)

0.4004 gram substance gave 56.1 cc. moist nitrogen at 22°.5 and 745.6 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	15.61

Methylphenylcyanamide, heated in a sealed tube with a slight excess of absolute alcohol, did not give a trace of the isourea ether, whereas carbodiphenylimide gives a nearly quantitative yield of the corresponding ether under the same treatment.

Some success attended the treatment of the cyanamide with 10 molecules of alcohol and 2 molecules of hydrogen chloride, but the reaction proceeds very slowly, reaching completeness only after several weeks, while with phenylcyanamide the action was complete in two days.

On heating ethyl methyl phenylisourea in a current of dry hydrogen chloride ethyl chloride was evolved. The residue left in the tube, after crystallization from low-boiling ligroin, melted at 81°, and mixed with the synthetically[2] prepared methyl phenylurea the melting-point was still 81°. The reaction took place according to

$$C_6H_5NCH_3.C(:NH)OC_2H_5 + HCl \rightarrow C_2H_5Cl + C_6H_5NCH_3CONH_2.$$

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[1] Stieglitz: Ber. d. chem. Ges., **28**, 573.

[2] Gebhardt: *Ibid.*, **17**, 2095.

Ethyl Methylphenylisourea Chlorplatinate, $(C_{10}H_{15}N_2O)_2PtCl_6$, made by adding a slight excess of an absolute alcoholic solution (1 : 1) of chlorplatinic acid to an ether solution of the ethyl methyl phenylisourea, forms brownish-yellow crystals.

0.4288 gram substance gave 0.1097 gram platinum.

	Calculated for $C_{20}H_{30}N_4O_2PtCl_6$.	Found.
Pt	25.43	25.58

The platinum salt melts at 160° with evolution of a gas, darkening in color a few degrees below its melting-point. While the form of the individual crystal could not be determined by the use of the microscope, that of the crystal aggregate is peculiar and distinctive, the crystals joining together to form an aggregate, which, under the microscope, has an appearance similar to that of a pine tree.

Action of Dilute Hydrochloric Acid on Ethyl Methylphenylisourea.

With the ethyl ether of methylphenylisourea, as in the case of the phenylisourea ethers, the first action, when heated with dilute hydrochloric acid, is the formation of alkyl chloride and a urea according to

$$C_6H_5N(CH_3)C(:NH)OC_2H_5 + HCl \longrightarrow C_6H_5N(CH_3)CONH_2 + C_2H_5Cl.$$

Experiment showed that, in addition to this fundamental reaction, the dilute acid brought about some saponification of the methylphenylurea with formation of methylaniline, as follows:

$$C_6H_5N(CH_3)CONH_2 + H_2O \longrightarrow C_6H_5.NH.CH_3 + NH_3 + CO_2.$$

The methylaniline thus formed was, to a very small extent, ethylated by the ethyl chloride present with formation of methylethylaniline,

$$C_6H_5.NH.CH_3 + C_2H_5Cl \longrightarrow C_6H_5N(C_2H_5)CH_3 + HCl.$$

Ethyl methylphenylisourea (1 mol.) was heated in a sealed tube with 8 per cent hydrochloric acid (1.1 mol.) for four hours at 100°. The tube opened with pressure due to ethyl chloride (green-edged flame). That saponification of the methylphenylurea with formation of methylaniline had taken place was shown by the fact that a portion of the liquid gave a yellow solution (nitrosomethylaniline) on the addition of a little sodium nitrite. For confirmation, parallel experiments were carried out with acid solutions of the urea ether and of the urea ether and methylaniline, only the latter giving the yellow color of the nitroso compound. The presence of a trace of methylethylaniline was shown by the yellow acid solution formed by sodium nitrite, after reduction with zinc, giving a blue color with ferric chloride and hydrogen sulphide.

Experiments carried out parallel to the one just given show that a mixture of isourea ether and methylaniline does not give the thionin color while a mixture of isourea ether, methylaniline, and dimethylaniline readily gives methylene blue. The presence of unchanged ethyl methylphenylisourea was shown by the fact that a portion of the solution, when reheated in a sealed tube at 100° for several hours, gave some more alkyl chloride. No attempt was made to isolate the methylphenylurea formed, owing to its extreme solubility.

Ethyl α-Methyl-α-diphenylisobiuret, $C_6H_5NCH_3.C(OC_2H_5):N.CONHC_6H_5$.—Ethyl methylphenylisourea was treated with slightly less than the equivalent amount of phenyl isocyanate. The solid separating from the cold solution was filtered off and washed with cold absolute ether. Recrystallized from a little warm alcohol, it melted at 115° to 116°, softening, but not melting, about 1° lower. The biuret is formed according to

$$C_6H_5NCH_3C(:NH)OC_2H_5 + C_6H_5NCO \rightarrow C_6H_5NCH_3.C(.OC_2H_5):NCONHC_6H_5.$$

When boiled with dilute hydrochloric acid, ethyl chloride is given off. It can be burned at the mouth of the test-tube.

The α-methyl-α-diphenylbiuret formed melted at about 102°.

Analysis of the ethyl ether gave the following figures:

0.1332 gram substance gave 16.55 cc. moist nitrogen at 17°.5 and 749.5 mm.

	Calculated for $C_{17}H_{19}N_3O_2$.	Found.
N	14.17	14.24

Action of Dilute Hydrochloric Acid on Ethyl α-Methyl-α-diphenylisobiuret.

The following experiments were made in order to determine if the action of dilute acid in the cold on a urea ether with more negative groups is the same as when the two are heated together for a shorter time.

Ethyl α-methyl-α-diphenylisobiuret was placed in a sealed tube with slightly more than the equivalent amount of normal hydrochloric acid and kept nine days at the ordinary temperature. The tube opened with no pressure, showing that only a minute quantity of ethyl chloride could be present. The solid melted at 101° to 102° after recrystallization from alcohol. It was probably the hitherto unknown biuret,

$$C_6H_5NCH_3CONHCONHC_6H_5,$$

but an analysis was not made. Ethyl alcohol could not be found in the filtrate from the biuret by the iodoform test. The presence of aniline was shown by the fact that the filtrate gave an isonitril odor when treated with chloroform and caustic potash, but did not give an alkaline gas when treated with caustic potash alone. The presence of methylethylaniline was suspected from the odor of the alkaline filtrate and proved by the thionin (methylene blue) test. The presence of these products is readily explained if the first action is considered as the formation of alkyl chloride and the biuret according to

$$C_6H_5NCH_3.COC_2H_5 : N.CONHC_6H_5 + HCl \longrightarrow C_6H_5NCH_3CONHCONHC_6H_5 + C_2H_5Cl,$$

and that a part of the biuret is then saponified, producing aniline and methylaniline, as follows:

$$C_6H_5NCH_3CONHCONHC_6H_5 + 2H_2O \longrightarrow C_6H_5NHCH_3 + C_6H_5NH_2 + 2CO_2 + NH_3.$$

The presence of a dialkylaniline shows that the ethyl chloride was employed in ethylation of the aniline and methylaniline according to

$$C_6H_5NH_2 + 2C_2H_5Cl \longrightarrow C_6H_5N(C_2H_5)_2 + 2HCl$$

and $$C_6H_5N(CH_3)H + C_2H_5Cl \longrightarrow C_6H_5N(CH_3)C_2H_5 + HCl.$$

When the isobiuret was heated with normal hydrochloric acid for three and a half hours at 100°, the products were the same as when the action took place in the cold, excepting that the tube opened with very slight pressure due to ethyl chloride. It may be concluded, therefore, that an increase of temperature does not change the course of the reaction with dilute acid, excepting that the time required for the completion of the reaction is shortened.

Methyl (asym)-Methylphenylisourea, (*Methyl Imidophenylmethylcarbamate*), $C_6H_5NCH_3C(: NH)OCH_3$, was prepared because it was thought that it might be a solid like some other methylisourea ethers, but the influence of the methyl group joined to nitrogen so lowers the melting-point that even at a temperature of —18° the ether could not be solidified.

The method of preparation from methylphenylcyanamide was the same as that used for the ethyl ether, but the yield was not quite so good, though satisfactory. Distilled *in vacuo* the greater part of the oil boiled at 120° at 11 mm. pressure. The identity of the body was proved by forming and analyzing the platinum salt.

0.1696 gram substance gave 0.0447 gram platinum.

	Calculated for $(C_9H_{13}N_2O)_2PtCl_6$.	Found.
Pt	26.40	26.36

Methyl (asym.)-Ethylphenylisourea (*Methyl Imidophenylethylcarbamate*), $C_6H_5NC_2H_5.C(: NH)OCH_3$.—The ready addition of alcohol to alkylphenylcyanamides by means of sodium alcoholate was confirmed by the action of sodium methylate on ethylphenylcyanamide.

Ethylphenylcyanamide has been prepared by Clöez and Cahours[1] from ethylaniline by the action of chlorcyanogen. For its preparation in quantity it was found best to desulphurize ethyl phenylthiourea[2] with alkaline lead acetate solution in the same manner that methylphenylcyanamide was prepared. It was found to boil at 153° (19 mm.).

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[1] Ann. Chem. (Liebig), **90**, 94.

[2] Gebhardt: Ber. d. chem. Ges., **17**, 2094.

0.2005 gram substance gave 33.7 cc. moist nitrogen at 16° and 748.9 mm.

	Calculated for $C_6H_5NC_2H_5CN$.	Found.
N	19.21	19.37

Methyl ethylphenylisourea was formed by treating 14.6 grams (1 mol.) ethylphenylcyanamide dissolved in 40 grams methyl alcohol with a methyl alcohol solution of sodium methylate (from 2.6 grams of sodium). The farther treatment was the same as for the preparation of its isomer, ethyl methylphenylisourea. Fractionated twice *in vacuo* the oil boiled at 126° under 15 mm. pressure. Analysis gave the following figures :

0.1604 gram substance gave 22.5 cc. moist nitrogen at 15°.5 and 747.8 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	16.18

Hydrochloride of Methyl Ethylphenylisourea, $C_6H_5NC_2H_5C(:NH)OCH_3.HCl$.—Dry hydrogen chloride was passed into a solution of the isourea ether in absolute ether, the precipitated hydrochloride filtered off, and after washing with ether, dried *in vacuo* over caustic potash and concentrated sulphuric acid. Methyl ethylphenylisourea hydrochloride is insoluble in benzene, ligroin, and ether, but soluble in other organic solvents. Its water solution is neutral to litmus and to methyl orange. The salt was found to melt at 107° with evolution of methyl chloride.

0.1240 gram substance required 5.80 cc. tenth-normal $AgNO_3$ (chromate indicator).

	Calculated for $C_{10}H_{15}N_2OCl$.	Found.
Cl	16.51	16.59

Action of Dilute Hydrochloric Acid on Methyl Ethylphenylisourea.

Methyl ethylphenylisourea was heated with slightly more than the equivalent amount of 8 per cent hydrochloric acid for four hours in the Victor Meyer water-bath. The tube opened with pressure due to methyl chloride, which burned with its characteristic green-edged flame. The contents of the tube, when treated as in the similar experiment with ethyl methylphenylisourea showed the presence of ethylaniline, methylethylaniline (only a trace), and unchanged methyl ethylphenylisourea.

II. The Oxygen Ethers of Urea.

While derivatives of the oxygen ethers of urea have been known for some time,[1] the mother-substances, the oxygen ethers of urea itself, $NH_2C(OR):NH$, were unknown before this work was undertaken. Of the usual methods[2] which suggested themselves for preparing these interesting bodies, the addition of alcohol to cyanamide was attempted first according to

$$NH_2CN + HOR \quad \longrightarrow \quad NH_2C(OR):NH,$$

because the work on the alphylcyanamides had shown the way for converting cyanamides into isourea ethers. The method proved entirely successful. It is expected, however, that since the properties of these bodies are now known they may be prepared by other convenient methods.[3]

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[1] *a.* Griess: Ztschr. f. Chemie, 1867, 534; J. prakt. Chem., [2], **4**, 295; Ber. d. chem. Ges., **15**, 448.

b. Cyclic isoureas, Gabriel: Ber. d. chem. Ges., **22**, 1150; **28**, 2937; Hirsch: Ber. d. chem. Ges., **23**, 966; Menne: Ber. d. chem. Ges., **33**; 658.

c. Cyclic isoureas from imidocarbonic esters, Sandmeyer: Ber. d. chem. Ges., **19**, 862; Seliwanow: Ber. d. chem. Ges., **26**, 425.

d. Uric acid ethers, E. Fischer: Ber. d. chem. Ges., **17**, 332, 335.

e. Ethyl isocarbanilide, Lengfeld and Stieglitz: Ber. d. chem. Ges., **27**, 926; this JOURNAL, **17**, 112. Stieglitz: Ber. d. chem. Ges., **28**, 573.

f. Bromdiphenylisoureas. Hantzsch and Mai: Ber. d. chem. Ges., **28**, 983.

g. Isocarbanilides, Dains: J. Am. Chem. Soc., **21**, 136.

h. Benzoyl alkylisoureas, Dixon: J. Chem. Soc. (London), 1899, 380; Wheeler and Johnson: This JOURNAL, **24**, 217.

i. Isourea ethers, Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1494; **33**, 807, 1517.

[2] See preliminary reports, Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1494; **33**, 807, 1517.

[3] Other methods will be tried in this laboratory as soon as possible, *e. g.* the action of alkyl halides on silver ureas, the preparation of cyanic ethers, CN.OR, and the addition of ammonia to them, the action of diazourethane on urea, and the saponification of benzoylmethylisourea, etc. J. STIEGLITZ.

Methylisourea Hydrochloride (*Hydrochloride of Methyliminocarbamate*), $NH_2C(:NH)OCH_3.HCl$.—Preliminary experiments showed at once that methylisourea is formed when cyanamide is treated with absolute methyl alcohol and dry hydrogen chloride. The residue, left on evaporation of the alcoholic solution in a vacuum desiccator over concentrated sulphuric acid and solid caustic potash, gave, when heated in a current of dry hydrogen chloride, some methyl chloride and urea, but not at all in quantities corresponding to a nearly pure compound. Great difficulties were met in obtaining the ether and its salts in a pure condition. On the one hand, a large number of experiments were made to find the best conditions for preparing the hydrochloride and, on the other hand, to obtain a pure product by fractional crystallization of the hydrochloride and by fractional distillation of the free base. Success in the first line made it unnecessary to follow the second. Passing over all the preliminary work, the method will be described which first gave the pure hydrochloride and which is suitable for preparing small quantities of the substance, and then the mode of preparation on a large scale will be briefly given.

Forty-three grams (1 mol.) of well-dried silver cyanamide,[1] 80 grams (15 mol.) absolute methyl alcohol, and 19 grams (3.1 mol.) dry hydrogen chloride, were allowed to react for five to eight days. At the end of this period, when the solution no longer gave the test for cyanamide with silver nitrate and ammonia, the silver chloride was filtered off and the solution evaporated to dryness *in vacuo* over sulphuric acid and solid caustic potash. A crust, containing most of the impurities, was generally left on the sides of the beaker. The greater portion of the residue consisted of almost pure, well-formed, quadrangular prisms of methylisourea hydrochloride formed according to

$$CN_2Ag_2 + CH_3OH + 3HCl \rightarrow NH_2C(:NH)OCH_3,HCl + 2AgCl.$$

The second method of forming the hydrochloride, which is to be preferred, if a large amount of the compound is desired, is as follows: 8.7 grams dry hydrogen chloride (1.08 mol.) is passed into a well-cooled solution of 10.5 grams cyanamide[1] (1 mol.) in 200 grams methyl alcohol (25 mol.) which has been distilled over sodium. After standing two days the reaction is complete, for no precipitate of silver cyanamide forms on testing a portion of the solution with ammonia and silver nitrate. The solution is concentrated in a distilling flask under reduced pressure at 35° until crystals begin to appear in the liquid. The evaporation is completed in a vacuum desiccator over concentrated sulphuric acid and caustic potash. The hydrochloride is obtained in about the same state of purity as when it is prepared by the first method.

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[1] Walther: J. prakt. Chem., [2], **54**, 510.

Syntheses by means of sodium alcoholate under various conditions were tried, but only traces of the desired isourea ether were obtained.

From a preparation of the salt from silver cyanamide some of the more perfect crystals were taken, washed with absolute alcohol, powdered, and after drying *in vacuo* over sulphuric acid and solid caustic potash for three days to remove any excess of hydrochloric acid analyzed (Analysis I). The alcohol used in washing the crystals for Analysis I also left, on evaporation, pretty crystals of pure hydrochloride (Analysis II). The crude salt prepared from cyanamide was dissolved in a small volume of absolute alcohol warmed to a temperature of 55° to 60°. When cooled to —10° this alcoholic solution gave crystals of the pure methylisourea hydrochloride (Analyses III and IV).

I. 0.1107 gram substance required 10.05 cc. tenth-normal $AgNO_3$ (chromate indicator).

II. 0.1149 gram substance required 10.41 cc. tenth-normal $AgNO_3$.

III. 0.1001 gram substance required 9.03 cc. tenth-normal $AgNO_3$.

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[1] Volhard: J. prakt. Chem., [2], 9, 25. It was found better after filtering from the mercuric sulphide and neutralizing with acetic acid to distil off almost all the water from the cyanamide at a pressure of about 25 mm. instead of evaporating on the water-bath to a small volume.

IV. 0.0785 gram substance gave 18.2 cc. moist nitrogen at 25° and 748.5 mm.

	Calculated for $C_2H_6N_2O.HCl$.	Found. I.	II.	III.	IV.
Cl	32.05	32.18	32.12	32.04	....
N	25.39	....	....	....	25.62

Besides proving the identity and purity of the new salt, the analyses brought out the noteworthy fact that methylisourea forms only a stable monohydrochloride.[1] This salt is perfectly neutral.[2] A little of the hydrochloride dissolved in water did not change the tint of neutral litmus paper. That an unstable higher hydrochloride probably exists is shown by the fact that the powder used for Analysis I, after having been in the desiccator but a short time gave, on analysis, 34.74 per cent chlorine. Its aqueous solution reacted strongly acid towards litmus and methyl orange.

Methylisourea hydrochloride is very soluble in water and in methyl alcohol, not quite so soluble in ethyl alcohol, and insoluble in ether. Heated in a melting-point tube, it melts at 132° to 133° with evolution of methyl chloride. When it was heated in a current of hydrogen chloride it melted at 130°, forming methyl chloride quantitatively; the residue, dissolved in water, gave, with a few drops of nitric acid, a good yield of urea nitrate melting at 161°. Mixed with synthetic urea nitrate the melting-point remained unchanged. These reactions and the method of formation prove the constitution of the substance to be that of the hydrochloride of the methyl oxygen ether of urea:

$$NH_2CN + CH_3OH + HCl \rightarrow NH_2C(:NH)OCH_3.HCl;$$
$$NH_2C(:NH)OCH_3.HCl \rightarrow NH_2CONH_2 + CH_3Cl.$$

Methylisourea Chlorplatinate, $[NH_2C(:NH)OCH_3]_2H_2PtCl_6$.—Some of the crude crystals of the hydrochloride were washed with a small amount of absolute alcohol and then dissolved in a little of the alcohol and an excess of an alcoholic solution of chlorplatinic acid added. As no crystals separated on cooling the solution to —10°, absolute ether was added. A precipitate formed which was filtered and washed with dry ether with the aid of the filter-pump. After drying *in vacuo* over concentrated sulphuric acid it was analyzed.

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[1] Stieglitz: This Journal, 21, 105.

[2] *Ibid.*, 106.

0.1917 gram substance gave 0.0668 gram platinum.

II. 0.2026 gram substance gave 17.5 cc. moist nitrogen at 12° and 754.0 mm.

	Calculated for $(C_2H_7N_2O)_2PtCl_6$.	Found. I.	Found. II.
Pt	34.92	34.85	....
N	10.07	....	10.20

The chlorplatinate is soluble in water, methyl and ethyl alcohols, and acetone. It crystallizes in long, lemon-yellow needles, which on heating become orange at about 120°, and melt at 178° with evolution of a gas.

Methylisourea,[1] $NH_2C(:NH)OCH_3$.—Three and two-tenths grams of methylisourea hydrochloride were placed in a flask with about 1 gram water and 20 cc. alcohol-free ether, and the whole cooled to —12°. Powdered caustic potash was then added in small portions, but in large excess (20 to 25 mol.). The ether was decanted off, fresh ether added, and brought into good contact with the nearly solid mass under it by rubbing with a glass rod, decanted off, and the addition of fresh ether repeated a third and a fourth time. The resulting ether solution was shaken five minutes with anhydrous sodium sulphate, filtered by means of a siphon filter, and most of the ether distilled off in the water-bath. On scratching with a glass rod the concentrated ether solution (cooled to —10°), a crystalline precipitate of the free methylisourea resulted. If the hydrochloride used was of good quality, the yield of pure methylisourea is practically quantitative. If impure hydrochloride is used, the product is best purified by distilling *in vacuo*. Recrystallized from absolute ether the melting-point was 44° to 45°.

0.2430 gram substance gave 0.2875 grams CO_2 and 0.1793 grams H_2O.

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[1] Other names are methyl imidocarbamate, methyl imidoamidoformate, and methoxyformamidine.

	Calculated for $NH_2.COCH_3:NH$.	Found.
C	32.37	32.27
H	8.17	8.27

Methylisourea distilled *in vacuo*, best in an Anschütz flask, boils at 82° at 9 mm. At atmospheric pressure it does not distil undecomposed. It has a fishy, amine-like odor and it is very volatile with the vapors of alcohol and of ether. This volatility is not unexpected when the relation of methylisourea, $NH_2C(:NH)OCH_3$, to methylurethane, NH_2COOCH_3, which is extremely volatile, is considered. Methylisourea is a very powerful base; its aqueous solutions react strongly alkaline and, as described above, it exactly neutralizes 1 molecule of hydrochloric acid, the monochloride giving a neutral solution with water. In accordance with that fact it was found that the base could be titrated against hydrochloric acid. The following determinations were made with freshly distilled methylisourea, using tenth-normal hydrochloric acid and methyl orange as indicator.

I. 0.1410 grams required 18.87 cc. tenth-normal HCl; calculated 19.02 cc.

II. 0.1488 grams required 19.94 cc. tenth-normal HCl; calculated 20.07 cc.

III. 0.0996 grams required 13.36 cc. tenth-normal HCl; calculated 13.43 cc.[1]

Considering the hygroscopic character of the base the titrations are as close to the theory as could be expected.

Attempts were made to isolate the free isourea ether by treating a methyl alcohol solution of the hydrochloride with the theoretical amount of sodium methylate, and, after filtering from the precipitated sodium chloride, distilling the resulting solution.[2] In each trial a large amount of the base went over with the methyl alcohol, making the distillate strongly alkaline. After distilling off the alcohol at reduced pressure a little oil was left, a few drops of which distilled on heating *in vacuo*, but the greater portion suddenly decomposed, giving a white solid.

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[1] This titration was made by placing a measured amount of acid in the flask, weighing, adding isourea ether, and weighing again, and titrating the excess of acid with tenth-normal sodium hydroxide.

[2] Lobry de Bruyn's method for preparing free hydroxylamine. (Rec. trav. chim. Pays-Bas., II., 18).

Methylisourea exposed to the air took up sufficient moisture within a few hours to dissolve it. After a couple of days all solvent had disappeared, leaving a solid, the greater part of which was the carbonate of the base, as was shown by identifying the gas evolved when it was treated with dilute acid. No urea could be detected by the furfurol test. A small amount of a solid insoluble in water and in dilute acid was formed, but it was not identified. The total weight of solid obtained was only half that of the methylisourea taken, owing to the great volatility of the isourea ether.

Action of Dilute Hydrochloric Acid on Methylisourea.

When heated with dilute aqueous hydrochloric acid, the simple isourea ethers, like their phenylated derivatives, give urea and an alkyl chloride. But at the same time, to a very small extent (about 1 per cent) a decomposition into methyl urethane[1] and ammonium chloride takes place according to

$$NH_2C(:NH)OCH_3 + H_2O + HCl \rightarrow NH_2COOCH_3 + NH_4Cl.$$

This decomposition is especially worthy of note from its correspondence to that of the imidoethers when they are treated with dilute acid.

Methylisourea and slightly more than the equivalent amount of normal hydrochloric acid were heated for three and a half hours in a Victor Meyer water-bath. The tube was opened to allow the escape of methyl chloride, resealed, and heated for three hours longer. On opening the second time there was again pressure due to alkyl chloride. Evidently the decomposition of the hydrochloride into methyl chloride and urea is a slow process, showing the salt to be a comparatively stable one even at high temperatures. In the time required to decompose the chloride, much of the urea formed is saponified to ammonia and carbonic acid, and the ammonia partly converted into methylamine. The solution was found to be alkaline. A portion of it was neutralized with a few drops of dilute nitric acid and titrated with silver nitrate. Fifty per cent of the chlorine originally in the solution was found still present in the ionic condition.

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[1] Proved exactly in the case of ethylisourea.

A second portion of the solution, when tested for methyl alcohol by the delicate resorcinol test,[1] gave negative results. The third and larger part of the solution was evaporated to dryness *in vacuo* over concentrated sulphuric acid. The solid remaining was extracted twice with absolute ether and the ether solution evaporated. A small amount of a solid was left. It melted at 43° and had the solubilities of methylurethane. The amount was too small to recrystallize, but from its low melting-point it was probably methylurethane, NH_2COOCH_3 (melting-point 52°). The solid which had been extracted with ether was dissolved in a little water and a few drops of nitric acid added; the resulting abundant precipitate was identified as urea nitrate.

Benzoylmethylisourea (*Methyl Imidobenzoylcarbamate*), $C_6H_5CONHC(:NH)OCH_3$,[2] was prepared by dissolving methyl isourea hydrochloride in an excess of a 10 per cent solution of caustic potash, adding slightly less than the equivalent amount of benzoyl chloride and shaking vigorously until no acid chloride remained unaffected. The benzoylmethylisourea was filtered off and purified by dissolving it in a little methyl alcohol and fractionally precipitating it by the careful addition of water to the cold solution. This recrystallized substance forms monoclinic prisms melting at 76°.5.[3] The yield was almost quantitative.

I. 0.2802 gram substance gave 0.6238 gram CO_2 and 0.1464 gram H_2O.

II. 0.1536 gram substance gave 21.5 cc. moist nitrogen at 18° and 738.4 mm.

	Calculated for $C_9H_{10}N_2O_2$.	Found. I.	Found. II.
C	60.61	60.72	....
H	5.67	5.86	....
N	15.76	....	15.77

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[1] Mulliken and Scudder: This JOURNAL, **21**, 266.

[2] Vide Dixon: J. Chem. Soc. (London), 1899, 380; Wheeler and Johnson: This JOURNAL, **24**, 217.

[3] Dixon gives the melting-point as 74° to 75°, Wheeler as 77°.

Benzoylmethylisourea is readily soluble in alcohol and ether. It acts both as a base and as an acid, dissolving easily in acids as well as in alkalies.[1] From the solution in alkalies careful addition of acid reprecipitates the benzoylmethylisourea, which was identified by its crystal form, melting-point, and behavior towards boiling dilute hydrochloric acid (see below). It also forms a silver salt. None of the salts with metals has been prepared as yet in a pure condition. It is intended to investigate them further. It is probable that they have the interesting constitution

$$C_6H_5C(OK) : N.C(: NH).OCH_3.$$

The solution of benzoylmethylisourea in dilute alcohol reacts neutral to litmus, and in view of the fact that it has both basic and acid properties the free substance may be a salt analogous to amidoacetic acid.

Action of Dilute Hydrochloric Acid on Benzoylmethylisourea.

Benzoylmethylisourea was dissolved in slightly more than 1 molecule normal hydrochloric acid and the tube heated in the Victor Meyer water-bath three hours and a half. The tube opened with very slight pressure, due to methyl chloride, as shown by the gas burning with a green flame. The precipitate was separated into benzoylurea and benzoic acid by dissolving the latter in sodium carbonate. The benzoylurea[2] melted at 200° and was soluble in caustic alkalies; the benzoic acid melted at 120°, and when mixed with some of known constitution gave the same melting-point. The filtrate gave no trace of methyl alcohol by the resorcinol test. On making the filtrate alkaline with caustic potash a gas was evolved, which was strongly alkaline to litmus. That this gas was at least in part methylamine was shown by the fact that another portion of the filtrate, when treated with chloroform and caustic potash, gave a strong isonitril odor.

The amount of methyl chloride obtained by the action of aqueous hydrochloric acid on the benzoylmethylisourea seemed so unusually small that, in consequence of the presence of methylamine, I was led to suspect that methyl chloride was really formed in large quantities, as in the case of other urea ethers, but had been largely used up in methylating some ammonia formed by decomposition of the urea. This view was fully confirmed by repeating the experiment and heating the isourea ether with dilute hydrochloric acid for only twenty minutes. The tube now opened with great pressure and gave abundant methyl chloride. Benzoylmethylisourea is therefore decomposed in the first instance by dilute hydrochloric acid[1] like the other isourea ethers into alkyl chloride and a urea according to the equation:

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[1] The latter fact does not seem to have been observed by Dixon and Wheeler.

[2] Zinin : Ann. Chem. (Liebig), 92, 404, describes benzoylurea as melting at about 200°. Wheeler, *Loc. cit.*, gives the melting-point at 214°.

$$C_6H_5CONHC(:NH)OCH_3 + HCl \rightarrow C_6H_5CONHCONH_2 + CH_3Cl.$$

For purposes of comparison benzimidoethyl ether was heated for several hours with normal hydrochloric acid under the same conditions and gave, as expected, no trace of ethyl chloride, but only ethyl benzoate and ammonium chloride according to

$$C_6H_5C(:NH)OC_2H_5 + HCl + H_2O \rightarrow C_6H_5COOC_2H_5 + NH_4Cl.$$

With normal hydrochloric acid at the room temperature benzoylmethylisourea gave, after eight days, the same products as at higher temperatures.

It is seen that, in spite of the presence of the strongly negative benzoyl group, and of the weak basic properties of the substance, the decomposition is not affected by the water present—hydrolysis seems to play no rôle in this action as in the case of the imidoesters. This is the more striking since the solution of the hydrochloride is strongly acid, *i. e.*, water dissociates the salt into the free base and free acid, but according to the observed products of decomposition it can have no further action on the free base. This conclusion is in complete agreement with Dixon's experiments with benzoylmethylisourea,[1] according to which the compound could be heated with 10 parts of water to 105° to 125° without any sign of change. I confirmed this important point for the question of hydrolysis by heating the body for three hours with five times its weight of water in a sealed tube in a Victor Meyer water-bath. On opening the tube, the isourea ester was recovered unchanged, no interaction with the water having occurred.

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[1] Wheeler and Johnson (This JOURNAL, **24**, 217), working with a different object in view, found that benzoylmethylisourea is rapidly decomposed in the same way by gently warming it with 20 per cent hydrochloric acid. In the above experiment very dilute acid was always used with a view of detecting a possible hydrolysis of the urea ether salts, corresponding to the hydrolytic decomposition of the imidoethers. A large excess of acid would suppress hydrolysis and favor the formation of the decomposition-products of the hydrochlorides (Stieglitz: This JOURNAL, **21**, 106). As a matter of fact, Mr. McCracken, working under the direction of Dr. Stieglitz, was able to prove that imidoethers, like methyl imidobenzoate, readily give alkyl chlorides in quantity when heated with concentrated *aqueous* hydrochloric acid in place of the dilute acid. The results of Mr. McCracken's investigation, carried out early in 1899, will be published later, the work having been temporarily interrupted.

Methyl Phenylisobiuret (*Methyl Phenylureidoimidoformate*, $(C_6H_5NHCON:)COCH_3.NH_2$.[2]—Six-tenths of a gram (1 mol.) of methylisourea hydrochloride was dissolved in a very little water, an equivalent amount of a strong solution of caustic potash added, and to the resulting solution 0.6 gram (0.9 mol.) phenyl isocyanate added. After shaking the cold solution until no isocyanate odor could be detected, the solid which had separated was taken up with a little ether. The ether solution was washed three times with small amounts of water to get rid of any unchanged methylisourea, and dried with anhydrous sodium sulphate. The drying agent was filtered off, most of the ether distilled in the water-bath, and to the concentrated ether solution, cooled to —10°, low-boiling ligroin added to precipitate the isobiuret. The yield was fair.

The phenylisobiuret can also be made by mixing absolute ether solutions of equivalent amounts of methylisourea and phenyl isocyanate. This method, however, calls for the isolation of the free methylisourea, while by the first method the hydrochloride can be used, which is a distinct advantage.

The crystals are four-sided prisms, having rather blunt pyramidal ends. They melt at 89°.5 to 90°.

0.1180 gram substance gave 22.7 cc. moist nitrogen at 20°.5 and 753.5 mm.

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[1] *Loc. cit.*

[2] See page 214.

	Calculated for $C_9H_{11}N_3O_2$.	Found.
N	21.80	21.86

Hydrochloride of Methyl Phenylisobiuret, $(C_9H_{12}N_3O_2)Cl$.—Half a gram of the methyl ether was dissolved in absolute ether and dry hydrogen chloride run into the cold solution. The precipitate was filtered, washed with absolute ether, and, after drying on a clay plate *in vacuo* over sulphuric acid and solid caustic potash, analyzed.

The analysis was made by dissolving in dilute alcohol, adding tenth-normal alkali to neutrality (nearly the theoretical amount calculated for complete hydrolysis was required), and then titrating with chromate indicator and silver nitrate.

0.1750 gram substance required 7.72 cc. tenth-normal $AgNO_3$.

	Calculated for $C_9H_{12}N_3O_2Cl$.	Found.
Cl	15.43	15.64

The hydrochloride melts at 133° with evolution of a gas.

Action of Dilute Hydrochloric Acid on Methyl Phenylisobiuret.

On boiling methyl phenylisobiuret with dilute hydrochloric acid, methyl chloride was given off and burned at the mouth of the test-tube. The solution, on cooling, gave crystals which, after recrystallization, melted at 156° to 156°.5. Analysis showed it to be α-phenylbiuret, formed according to

$$C_6H_5NHCONH.COCH_3(:NH) + HCl \rightarrow CH_3Cl + C_6H_5NHCONHCONH_2.$$

Again, in spite of the fact that the hydrochloride is almost completely decomposed by water, water does not enter into the products of the decomposition.

α-Phenylbiuret, $C_6H_5NHCONHCONH_2$.—That the crystals melting at 156° to 156°.5 were α-phenylbiuret, as expected, was confirmed by the following analysis :

0.0793 gram substance gave 16.8 cc. moist nitrogen at 25° and 747.2 mm.

	Calculated for $C_8H_9N_3O_2$.	Found.
N	23.50	23.38

Its constitution follows from the method of preparation.

There is a phenylbiuret described in the literature,[1] but its constitution has not been determined and the properties given are general ones and are not specific enough to permit one to determine if it is identical with the one melting at 156° to 156°.5.

α-Phenylbiuret is soluble in alcohol, but almost insoluble in ether. It is best recrystallized from hot water, in which it is quite soluble.

Hydrochloride of Ethyl Isourea (*Ethyl Imidocarbamate Hydrochloride*, $NH_2C(:NH)OC_2H_5.HCl$.—Eight and nine-tenths grams (1 mol.) cyanamide were dissolved in 275 grams (30 mol.) absolute alcohol, which had been freed from water by distillation over sodium; into this solution there were passed 9.3 grams (1.25 mol.) dry hydrogen chloride, the flask and contents being kept cold by ice during the absorption of the gas. After four days the solution no longer gave a test for cyanamide with ammoniacal silver nitrate. The greater portion of the solvent was distilled off at reduced pressure, the temperature not rising above 35°, and the solution then evaporated *in vacuo* over sulphuric acid and solid caustic potash. When near dryness the mother-liquor was separated from the crystals which had formed. The crystals thus obtained were transparent, rhombic plates, which, if pure, gave a neutral solution when dissolved in water. Analysis of these neutral crystals showed that they were ethylisourea monohydrochloride (Analysis I). Generally the salt was not so pure and required recrystallization before analysis. Unlike the hydrochloride of the methyl ether it could not be readily crystallized from alcohol, owing to its greater solubility in that solvent. But on treating the alcohol solution fractionally with ether the hydrochloride was precipitated. It showed at first a somewhat high percentage of chlorine (28.94 per cent), but after remaining for some time (ten days) in a vacuum over solid caustic potash, it gave a neutral reaction and analysis showed it to be pure (II). Allowed to remain in a vacuum over caustic potash for a longer period, it showed no further change in composition (III and IV). In the analysis for nitrogen the combustion was carried out very slowly in order to prevent ethylene from passing over unburned and giving too high a percentage of nitrogen.

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[1] Weith: Ber. d. chem. Ges., 10, 1744.

I. 0.2561 gram substance required 20.54 cc. tenth-normal $AgNO_3$.

II. 0.1638 gram substance required 13.18 cc. tenth-normal $AgNO_3$.

III. 0.1339 gram substance required 10.75 cc. tenth-normal $AgNO_3$.

IV. 0.1016 gram substance gave 19.7 cc. moist nitrogen at 16°.5 and 761 mm.

	Calculated for $NH_2.C(:NH).OC_2H_5.HCl$.	Found. I.	II.	III.	IV.
Cl	28.45	28.43	28.52	28.47	....
N	22.53	....	....	....	22.68

The hydrochloride of ethylisourea melts at 123° to 124° with evolution of ethyl chloride.

Ethylisourea Chlorplatinate, $(NH_2.COC_2H_5:NH)_2H_2PtCl_6$.—Solutions of ethylisourea hydrochloride and chlorplatinic acid in absolute alcohol were cooled to —10° and mixed. Scratching with a glass rod caused the chlorplatinate to be partially precipitated. Absolute ether was added to complete the precipitation.

The crystals are at first translucent, four-sided, dark-yellow plates, which after a few minutes become of a lighter color and opaque, as if a loss of alcohol of crystallization had occurred.

This change in the appearance of the crystals can be very readily followed under the microscope. The chlorplatinate tends to come out as an oil, unless the solution from which it is precipitated is quite cold. Analysis of three different preparations gave the following figures :

I. 0.0887 gram substance gave 0.0298 gram platinum.

II. 0.1522 gram substance gave 0.0505 gram platinum.

III. 0.1361 gram substance gave 0.0454 gram platinum.

	Calculated for $(NH_2.COC_2H_5:NH)_2H_2PtCl_6$.	Found. I.	II.	III.
Pt	33.25	33.60	33.18	33.36

The chlorplatinate is soluble in water, alcohol, and chloroform, but insoluble in ether. Heated in a melting-point tube it melts with decomposition at 178°.5.

Ethylisourea (*Imido Ethylcarbamate*),[1] $NH_2C(:NH)OC_2H_5$.—The free ethylisourea was obtained from the hydrochloride by the same method as was used in the preparation of methylisourea.

Ethylisourea is more soluble in ether than the methyl compound, and readily forms supersaturated solutions in that solvent, so that severe cooling and vigorous scratching with a glass rod are sometimes necessary to start the crystallization from the solution from which most of the ether has previously been distilled off. The yield is satisfactory, but not quantitative as in the case of the methyl compound.

The base was titrated against tenth-normal hydrochloric acid, using methyl orange as the indicator.

0.1551 gram substance required 17.52 cc. tenth-normal HCl; calculated 17.59 cc.

0.1702 gram substance required 19.18 cc. tenth-normal HCl; calculated, 19.30 cc.

0.2839 gram substance gave 0.4249 gram CO_2 and 0.2290 gram H_2O.

	Calculated for $C_3H_8N_2O$.	Found.
C	40.83	40.82
H	9.17	9.04

Ethylisourea distils *in vacuo* at 89° under a pressure of 10.5 mm., and at 95° to 96° at 15 mm. Some of the pure solid kept in a closely-stoppered bottle six weeks was found to have partially liquefied. Lack of time prevented the determination of the decomposition-products.

Ethylisourea is a strong base, its aqueous solution reacting strongly alkaline. Such a solution added to a solution of copper sulphate precipitates copper hydroxide. If an excess of the isourea ether is added the hydroxide redissolves, forming a purplish-blue solution. Ethylisourea, added to a solution of aluminium sulphate, first precipitates the hydroxide, but an excess of the isourea redissolves the precipitate. Parallel test-tube experiments with aluminium sulphate and equivalent amounts of ethylisourea and ammonia gave results showing that ethylisourea is a considerably stronger base than ammonia.[1] As one might expect from the general similarity to ammonia, an aqueous solution of ethylisourea dissolves silver chloride.

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[1] Other names are ethoxyformamidine and ethyl imidoamidoformate.

Action of Dilute Hydrochloric Acid on Ethylisourea.

An experiment carried out with ethylisourea parallel to that with methylisourea and hydrochloric acid[2] gave the analogous decomposition-products; ethyl chloride, urea, and a small amount of ethylurethane, $NH_2COOC_2H_5$. The amount of urethane found was slightly more than 1 per cent of the theoretically possible amount; without recrystallization it melted at 44° to 45°, and when it was mixed with Kahlbaum's synthetic ethylurethane (melting-point 49° to 50°) the melting-point was raised to 46° to 47°. The iodoform reaction failed to show the presence of ethyl alcohol.

Ethyl Phenylisobiuret (*Ethyl Phenylureidoimidoformate*), $C_6H_5NH.CO.NH.COC_2H_5 : NH$, was prepared in the same manner as the methyl phenylisobiuret, except that it was found better to recrystallize it by adding water to its solution in a small volume of methyl alcohol. Thus precipitated, the compound gives monoclinic prisms melting at 85°.5 to 86°. The yield was good.

The Hydrochloride of Ethyl Phenylisobiuret, $C_6H_5NHCONH.COC_2H_5 : NH.HCl$, was prepared by treating the ethyl ether with dry hydrogen chloride in ether solution. It melts with decomposition at 141°.

Analysis of the hydrochloride was made by dissolving it in dilute alcohol, adding alkali to neutrality (the salt was strongly hydrolyzed), and titrating with silver nitrate and chromate indicator.

0.3319 gram substance required 13.51 cc. tenth-normal $AgNO_3$.

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[1] Quantitative determinations of the strength of the various classes of isourea-ethers and imidoethers will be made. J. STIEGLITZ.

[2] See page 249.

	Calculated for $C_{10}H_{14}N_3O_2Cl$.	Found.
Cl	14.55	14.43

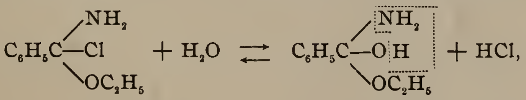
Action of Dilute Hydrochloric Acid on Ethyl Phenylisobiuret.

Ethyl phenylisobiuret was heated at 100° for three and a half hours with normal hydrochloric acid. The tube opened with pressure due to ethyl chloride. The solid was recrystallized from hot water and identified as phenylbiuret[1] by its melting-point and solubilities.

No ethyl alcohol could be detected in the filtrate by the iodoform reaction. That saponification of a part of the biuret had occurred, giving rise to aniline and ammonia, was shown by the filtrate giving with caustic potash an alkaline gas, and with chloroform and caustic potash a strong isonitril odor.

III. The Hydrolysis of the Hydrochloride of Ethyl Imidobenzoate and of the Hydrochloride of Ethyl Phenylisourea.

The difference in behavior towards water[2] of the hydrochlorides of the imidoethers, RC(: NH)OR, and the hydrochlorides of the urea ethers, RNHC(: NH)OR, forms one of the most interesting problems for investigation in this series of compounds, as the solution of this problem must have an important bearing on the determination of the constitution of the salts of imidoethers, etc.,[3] and on the whole subject of ester saponification.[4] The difference at the first glance[3] seems to be due to the difference in the strength of the imidoethers and urea ethers as bases: the salts of the weaker bases, the imidoethers, suffer hydrolysis to some extent, according to



$$C_6H_5C\begin{cases}NH_2\\Cl\\OC_2H_5\end{cases} + H_2O \rightleftharpoons C_6H_5C\begin{cases}NH_2\\OH\\OC_2H_5\end{cases} + HCl,$$

and give the decomposition-products of the hydrolyzed substance, *viz.*, ammonia and ethyl benzoate, the chlorides of these imidoethers being stable at ordinary temperatures. If the salts of the stronger bases, the urea ethers,

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[1] Page 254.

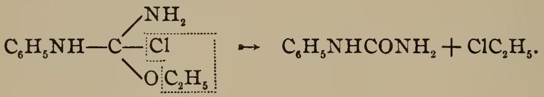
[2] Page 210.

[3] Stieglitz: This JOURNAL, **21**, 101.

[4] *Ibid.*; Ber. d. chem. Ges., **32**, 1494.

$$C_6H_5NHC(:NH)OR,$$

are not hydrolyzed, no decomposition would occur at ordinary temperatures, the chlorides being stable. And when decomposition is effected at higher temperatures in aqueous solution alkyl chloride and a urea would result, the decomposition-products of the salt



$$C_6H_5NH{-}\overset{NH_2}{C}{-}Cl\underset{OC_2H_5}{} \rightarrow C_6H_5NHCONH_2 + ClC_2H_5.$$

These considerations would give us a simple and rational explanation of the difference in behavior of the two series of salts. In confirmation of this view it was shown qualitatively that imidoether salts dissolve in water with an acid reaction,[1] the urea ether salts $C_6H_5NH.C(:NH)OC_2H_5.HCl$ and $NH_2C(:NH)OC_2H_5.HCl$, give solutions perfectly neutral to sensitive litmus paper.[1] It seemed of particular importance, however, to investigate the subject from a quantitative point of view. A series of experiments has been completed by Mr. Wm. McCracken under the direction of Professor Stieglitz,[3] showing the close connection between the velocity of decomposition or saponification of two or three imidoethers and their strength as bases—ethyl imidobenzoate, ethyl imido-*m*-nitrobenzoate, and ethyl imido-*m*-brombenzoate being used; and this work is now being continued by Mr. J. W. Shepherd. The determination of the affinity constants of the imido and urea ethers and of the conductivity of their salt solutions[4] will be included in this investigation.[5] As a preliminary quantitative study, I have undertaken to compare the extent of the hydrolysis of a typical imidoether salt, the hydrochloride of ethyl imidobenzoate, $C_6H_5C(:NH)OC_2H_5.HCl$, with that of a typical urea ether salt, the hydrochloride of ethyl phenylisourea, $C_6H_5NHC(:NH)OC_2H_5.HCl$, by titrating the free acid formed according to the equation

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[1] Stieglitz: This JOURNAL, 21, 106.

[2] This paper, pp. 217 and 210.

[3] See foot-note p. 209.

[4] To determine the extent of hydrolysis.

[5] A particular study will have to be made of the salts of acylated urea ethers, which readily give off hydrochloric acid on being dissolved in water and still give alkyl chlorides and acylated ureas as the final decomposition-products.

J. STIEGLITZ.

$$C_6H_5C(NH_2)(OC_2H_5)Cl + H_2O \rightleftarrows C_6H_5C(NH_2)(OC_2H_5).OH + HCl.$$

This method, as is well known, does not show the absolutely correct degree of hydrolysis: with the salts of very weak bases, in fact, it cannot be used at all, since the hydrolysis continues long after the originally free acid is neutralized, until nearly all of the salt is decomposed.[1] However, with salts of tolerably strong bases and an indicator, methyl orange, which is very sensitive to hydroxyl ions, the method does give results sufficiently reliable for preliminary purposes of comparison. This follows from the fact that neutral solutions result when even very small amounts of alkali (two or three drops of tenth-normal solution) are added to the salt solution. It also follows from these considerations: hydrolysis is caused according to the above equation primarily because the dissociation constant of the base is smaller than that of hydrochloric acid. For

$$C_6H_5C(NH_2)OH(OC_2H_5) \rightleftarrows \overset{+}{C_6H_5C(OC_2H_5)NH_2} + \overset{-}{OH},$$

$$\frac{P \times OH}{m} = k',$$

where *P*, *OH*, and *m* denote respectively the concentrations of the positive imidoether ions, the hydroxyl ions, and the undissociated molecules, and *k'* the ionization constant.

Where *k'* is very much smaller than the ionization constant for hydrochloric acid, *m* must always be in very large excess over *OH*, and, as the neutralization of the hydrogen ions of the acid proceeds, the new hydroxyl ions produced from water will continue to form large quantities of the undissociated base *m*, releasing an equivalent number of new hydrogen ions. But when *k'* approaches the constant for hydrochloric acid, this is, of course, not the case; with the formation of a moderately small additional amount of the molecular base *m*, k' can be fulfilled and the solution become alkaline very easily. When k' equals k_{HCl}, as for sodium hydroxide, the first drop of alkali produces alkalinity, as in the case of sodium chloride.

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[1] J. Walker: Ztschr. phys. Chem., 4, 319.

The following results are to be considered, therefore, only as close approximations to the determination of the true degree of hydrolysis,[1] but they fulfil the purpose for which this preliminary study was undertaken. The results show plainly:

1. That the hydrochloride of ethyl imidobenzoate is hydrolyzed by water, and that the amount of hydrolysis in the concentration used (approximately twelfth-normal) is somewhat less than 1 per cent of the total salt.

2. That the hydrochloride of ethyl (and methyl) phenylisourea is not hydrolyzed at all (concentration approximately twelfth-normal).

3. That ethyl imidobenzoate must be a fairly strong base ionizing quite easily, and that the hydroxide

$$C_6H_5C(OC_2H_5)(NH_2)OH$$

(ionized), must form readily, more readily, for instance, than $C_6H_5NH_3OH$ (ionized).

4. That ethyl phenylisourea is a still stronger base, whose affinity constant will most likely be found to be close to that of potassium or sodium hydroxide.

The determinations were made by dissolving a known weight of the free ethers[2] in an excess of carefully standardized tenth-normal acid and titrating back the excess of acid with tenth-normal sodium hydroxide, the final concentration of the salt solutions being about one-twelfth normal. In the first determinations (1 to 4 and 9 to 14) the weighings and titrations were made in a large glass-stoppered weighing-bottle. Later it was found better to make the weighings in glass bulbs in order to avoid loss by evaporation, and to use a widemouthed bottle for the titrations, the bulbs being broken by pressing with a heavy glass rod. In all the titrations methyl orange was the indicator used to determine the neutrality-point. The temperature was that of the laboratory, the determinations being made parallel to each other, at the same time. As a measure of precaution, the ethyl phenylisourea was distilled *in vacuo* just before using it. This seems not to have been necessary, for practically the same results were obtained from some of the ether which had stood in a desiccator for nearly a month.

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[1] More accurate results are expected from the determinations of the conductivity of the salt solutions. The calculation of the constants for hydrolysis has been postponed until the completion of these determinations.

[2] The free benzimidoether was prepared according to Bushong (this JOURNAL, 18, 490).

In titrations 13 to 18 the ethyl imidobenzoate had stood for some days in a desiccator; for titrations 19 to 21 it was freshly distilled, that boiling at 106°.5 to 107° at 15.5 mm. being taken. In order to be more certain of its purity it was analyzed.

0.2787 gram substance gave 0.7376 gram CO_2 and 0.1899 gram H_2O.

	Calculated for $C_9H_{11}NO$.	Found.
C	72.41	72.18
H	7.45	7.64

Several determinations were also made with methyl phenylisourea (titrations 9 to 12).

A drop of tenth-normal acid makes a difference of about 0.2 per cent; the error of weighing is about a fourth as much.

The average amount of hydrolysis found for ethyl phenylisourea was 0.13 per cent (titrations 1 to 8); for the methyl ether 0.058 per cent (titrations 9 to 12). Both of these results are within the limit of error of the experiment and indicate that most likely no hydrolysis occurs with these isourea ethers.

In the case of ethyl imidobenzoate, omitting titration 20, which is obviously out of harmony with the others, the average found was 0.925 per cent. Mr. McCracken,[1] using a somewhat different method, found approximately 2 per cent hydrolysis in one-twentieth normal dilution and 1.3 per cent in one-fifth normal solutions.

In conformity with these results I found that the hydrochlorides of methyl[1] and ethyl[2] phenylisourea dissolve in water, giving solutions perfectly neutral to sensitive litmus.

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[1] Pages 209 and 260.

Ethyl imidobenzoate hydrochloride gives an acid solution,[3] as is well known.

	Grams substance taken.	Calculated No. cc. N/10 HCl.	Found No. cc. N/10 HCl.	Final No. cc. solv'nt.	Percentage hydrolysis.
		Ethyl Phenylisourea.			
1	0.3884	23.654	23.583	26	0.30
2	0.4151	25.280	25.167	28	0.45
3	0.4253	25.901	25.875	31	0.10
4	0.4534	27.612	27.587	31	0.09
5	0.3231	19.677	19.671	22.5	0.03
6	0.2793	17.009	17.006	19	0.02
7	0.5087	30.980	30.904	34	0.24
8	0.3763	22.917	22.961	26.5	—0.19
				Average,	0.13
		Methyl Phenylisourea.			
9	0.4156	27.670	27.712	29	—0.15
10	0.4984	33.187	33.070	35	0.32
11	0.2722	18.112	18.123	20	—0.06
12	0.3653	24.324	24.293	27	0.13
				Average,	0.058
		Ethyl Imidobenzoate.			
13	0.2724	18.263	18.066	19.5	1.08
14	0.2801	18.779	18.582	20	1.05
15	0.4076	27.328	27.001	33	1.20
16	0.3901	26.154	25.948	33	0.79
17	0.3515	23.567	23.437	27	0.98
18	0.2986	20.020	19.840	23.5	0.90
19	0.3633	24.365	24.185	26	0.74
[20	0.3256	21.834	21.425	25	1.87]
21	0.5052	33.872	33.648	35.5	0.66
				Omitting [20], average,	0.925

The above investigations were carried out under the direction of Dr. Julius Stieglitz, and I wish to express here my sincere thanks for the personal interest he took in the work and the thoughtfulness with which he guided it.

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[1] Page 229.

[2] Page 217.

[3] Stieglitz : This JOURNAL, **21**, 106.

Contributions from the Sheffield Laboratory of Yale University.

LXXX.—ON THE PURIFICATION OF CAESIUM MATERIAL.

By H. L. Wells.

Several years ago[1] I recommended the use of the yellow salt $2CsCl.PbCl_4$ as a means of precipitating caesium from its solutions. Subsequent experience has shown that the method is very convenient for removing small quantities of the rare metal from all sorts of solutions; particularly from those from which the greater part of it has been precipitated by other means. For large quantities of caesium, however, the lead tetrachloride method, used alone, is inconvenient on account of the large amount of chloride that must be used, and because it is possible to obtain only very dilute solutions of lead chloride or of the white double salt, $CsCl.2PbCl_2$.[2]

I have used extensively the salt just mentioned as a means of precipitating caesium from concentrated solutions of the crude extract of pullucite, made by means of hydrochloric acid. The precipitation is made by adding a hot concentrated solution of the calculated amount of lead nitrate. The precipitate is crystalline and can be readily washed with dilute hydrochloric acid; then it can be very easily decomposed by boiling with ammonium carbonate solution. The method is satisfactory in a case where very little potassium and practically no rubidium are present, for, although it does not give a good separation from these metals, the precipitation of caesium is nearly complete. The precipitate $CsCl.2PbCl_2$, however, is very heavy compared with the amount of caesium that it contains, and its decomposition with ammonium carbonate produces 4 molecules of ammonium chloride for 1 of caesium chloride. For these reasons the method has been abandoned in this laboratory in favor of the method of Godeffroy.

In precipitating caesium according to Godeffroy's method I am accustomed to use less concentrated hydrochloric acid solutions than those that have been recommended. About one-third or one-half of the total volume of concentrated hydrochloric acid answers very well, and a solution of this kind possesses the advantage that it can be filtered by means of paper. To such a solution antimony trichloride, also dissolved in hydrochloric acid, is added as long as a precipitate forms. The latter is collected, best on a Büchner filter, and well washed with cold dilute hydrochloric acid.

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[1] Am. J. Sci., (3), 46, 186.

[2] *Ibid.*, (3), 45, 121.

To the filtrate and washings from the antimony salt, without concentrating them, lead nitrate is added at the rate of 2 or 3 grams per liter. This salt should be dissolved in water before it is added. Chlorine gas is then passed in until the solution is saturated with it. After standing for a few hours the liquid is decanted from the precipitate of the salt Cs_2PbCl_6 (which is usually colored green from the presence in it of the dark-blue salt Cs_2SbCl_6),[1] and is tested by the addition of a little more lead nitrate, and chlorine also if necessary. This precipitation is so complete, as far as caesium is concerned, that the liquid may be finally discarded. A liter of such a liquid will probably hold in solution only about 0.1 gram of the salt Cs_2PbCl_6, but the rubidium salt is nearly one hundred times more soluble. The lead tetrachloride salt should be washed on a Büchner funnel with cold dilute hydrochloric acid.

Formerly I was accustomed to decompose the antimony salt, $3CsCl.2SbCl_3$,[2] by suspending it in water and passing in hydrogen sulphide gas, but for large quantities this is a very slow and laborious operation, and it is much more convenient to treat it in a large porcelain dish with boiling dilute ammonium hydroxide. The antimonious oxide thus produced is dense and easy to filter and wash; moreover, it may be readily dissolved in hydrochloric acid and used again for precipitating caesium. A little antimony goes into solution in the ammonia, but this is readily removed, best after the liquid has become slightly acid by evaporation, by passing in hydrogen sulphide and filtering.

[1] Concerning this compound see the next article.

[2] The composition of this compound was very incorrectly determined by Godeffroy, who gave it the formula $6CsCl.SbCl_3$. Setterberg first arrived at the correct formula, which was afterwards confirmed by Remsen and Saunders, and also by Muthmann, and by Wells and Foote.

The removal of ammonium chloride on a large scale by ignition is a very slow operation. It is therefore best, in most cases, after the hydrogen sulphide has been removed by evaporation, to add to the concentrated solution of caesium and ammonium chlorides, in a large porcelain dish, a liberal amount of concentrated nitric acid and to heat cautiously until frothing has ceased. When further additions of strong nitric acid produce no change of color nor evolution of gas upon heating, the ammonium salts are entirely destroyed and the caesium chloride changed to nitrate.[1] The solution of caesium nitrate in nitric acid is then evaporated to dryness, and the residue is heated until the acid nitrate[2] is decomposed and the normal nitrate is more or less completely fused. The evaporation of the nitrate to dryness in the presence of nitric acid over a free flame in a dish is not a difficult operation, since decrepitation takes place to a much less extent than is the case when the chloride is evaporated in the same way. A large mass of fused caesium nitrate should not be allowed to solidify quietly in the bottom of a porcelain dish, for on cooling it is liable to break the dish by its contraction. If it is stirred as it solidifies this danger is avoided.

Caesium nitrate is one of the most beautiful of salts for recrystallization. Like potassium nitrate, it is much more soluble in hot water than in cold, and it crystallizes upon slowly cooling a hot concentrated solution in the form of large, colorless prisms. I have found that recrystallizing this salt tends to purify it from traces of rubidium, for a large quantity of the salt which showed no rubidium spectrum, upon systematic recrystallization, showed a distinct spectrum for that metal in the final mother-liquor. This, however, is a slow method of purification if it is desired to carry the latter to the last degree, but the nitrate obtained by one or two recrystallizations is pure enough for any ordinary purpose, unless the original antimony salt was contaminated to an unusual extent.

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[1] This method of destroying ammonium chloride is due to J. Lawrence Smith. See Am. J. Sci., (2), 34, 367.

[2] A description of the acid caesium nitrates will soon be published from this laboratory.

The nitrate is readily converted into carbonate by mixing it with 2 parts of pure oxalic acid, adding a little water, evaporating to dryness, and fusing the residue in a platinum crucible.[1]

Where the highest degree of purity in a caesium salt is desired, the salt $CsCl_2I$,[2] by its recrystallization, probably offers one of the best means for accomplishing that object. It is very much less soluble than the corresponding rubidium, potassium, sodium, and lithium salts. I have found that this salt may be made very conveniently from the nitrate by dissolving one part of the latter together with one atomic proportion of iodine in about 10 parts of 1 : 1 hydrochloric acid at a temperature just below boiling. The solution takes place quickly, and, upon cooling, the beautiful yellow salt crystallizes out. It is recrystallized by solution in hot 1 : 1 hydrochloric acid and cooling. One or two recrystallizations, when each crop is well drained and washed with a little cold dilute hydrochloric acid, give, even from impure materials, a remarkably fine product. From this trihalide by ignition, best at a very gentle heat so that the mass does not fuse, pure caesium chloride may be prepared.

APRIL, 1901.

LXXXI.—ON A SALT OF QUADRIVALENT ANTIMONY.

BY H. L. WELLS AND F. J. METZGER.

While engaged in purifying some caesium material we precipitated a large quantity of the salt $Cs_3Sb_2Cl_9$ by adding an excess of antimony trichloride to a hydrochloric acid solution of impure caesium chloride. A small amount of caesium remained in the filtrate, and, wishing to recover this, we added a solution of lead nitrate and passed chlorine gas into the liquid in order to precipitate the very insoluble lead tetrachloride salt, Cs_2PbCl_6.[3] Much to our surprise the precipitate, while showing the usual octahedral form, was bright-green in color, whereas the pure lead salt is bright-yellow. The product was found to contain a small quantity of antimony, and by preparing the lead salt after the addition of varying quantities of antimony trichloride we obtained products of various colors, from yellowish-green to dark bluish-green. The following determinations were made in a lighter and a darker product:

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[1] Method of J. Lawrence Smith, *Loc. cit.*

[2] Am. J. Sci., (3), 43, 17.

[3] *Ibid.*, (3), 46, 180.

	Light-green. Per cent.	Dark-green. Per cent.
Sb	0.92	1.44

These results indicated that antimony was not an essential constituent of the compound, and it seemed probable that some salt of antimony isomorphous with the salt Cs_2PbCl_6 had crystallized with it. We drew the further inference that the isomorphous antimony compound must be strongly colored, probably blue. Fortunately we had access to the reprint of an article by Setterberg[1] (which, as far as we can find, has not been noticed in any of the books of reference), where a peculiar black caesium-antimony salt is described. Setterberg made this compound by boiling a solution of antimony trichloride in strong hydrochloric acid with antimony pentachloride and caesium chloride in excess. He ascribes to it the formula $2CsCl.SbCl_4$ or $4CsCl.SbCl_3.SbCl_5$, and states that it forms black, very small, short prisms. It was evident that a salt of this composition might be expected to crystallize with one of the composition $2CsCl.PbCl_4$, and if so the fact would be a strong argument in favor of Setterberg's first formula, but his description of the form of the salt gave no evidence of the isomorphism of the two compounds.

We have prepared Setterberg's salt under varying conditions, and have confirmed his formula, as is shown by the following analysis of a very pure product:

	Calculated for Cs_2SbCl_6.	Found.
Cs	44.41	44.92
Sb	20.03	20.23
Cl	35.56	35.13
	100.00	100.28

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[1] Öfversigt K. Vetensk-Akad. Förhandl., 1882, 23.

As far as can be judged by careful microscopic examination this salt crystallizes in perfect octahedra. We could find no indication of a prismatic form corresponding to Setterberg's description, hence it is probable that his crystals were so small that he did not make them out clearly. No optical examination of the crystals could be made on account of their complete opacity. The color of the crystallized substance is absolutely black, but when a little of it is rubbed between the ground surfaces of a glass-stoppered bottle it shows a very strong, dark-blue color.

From the crystalline form and color of this curious salt there can be no doubt that it was the substance which gave the green color to our products of the salt Cs_2PbCl_6, and it seems certain that the two salts are isomorphous. The color of the antimony salt indicates that it is not a compound containing antimony trichloride and pentachloride, for the known caesium double salts with these chlorides, $3CsCl.2SbCl_3$ and $CsCl.SbCl_5$,[1] are colorless or nearly so.

We are convinced, therefore, that this black salt, Cs_2SbCl_6, is a member of the well-known group of octahedral double halides of quadrivalent elements, among which are K_2PtCl_6, Cs_2SnCl_6, Cs_2TeCl_6, Cs_2TeI_6, K_2PbCl_6, and Cs_2PbCl_6, and that it is a double salt of antimony tetrachloride, $SbCl_4$.

Judging from the color of the double salt, the tetrachloride, $SbCl_4$, must be black. This color would be entirely unexpected, since the chlorides $SbCl_3$ and $SbCl_5$ are colorless. We have tried in vain to get some evidence of the separate existence of a black chloride by making mixtures of the two known chlorides at low and high temperatures and by treating the salt Cs_2SbCl_6 with cold concentrated sulphuric acid.

The oxide of antimony, Sb_2O_4 or SbO_2, is usually regarded as a compound of Sb_2O_3 and Sb_2O_5. It is possible that this may be a true dioxide, but it would be expected that an oxide which corresponded to a black chloride would be black also, for, if there is a difference in color, oxides are usually darker than the corresponding chlorides.

We have prepared a jet-black double bromide by using a method exactly like that by means of which the black double chloride was made. Judging from analogy, this is probably the salt Cs_2SbBr_6, but we were unable to get a product that was pure enough for analysis, as it was always mixed with more or less light-colored impurity. We attempted, without success, to make the corresponding iodide and fluoride.

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[1] Setterberg: *Loc. cit.*

APRIL, 1901.

LXXXII.—ON THE ACID NITRATES.

BY H. L. WELLS AND F. J. METZGER.

A number of years ago it was noticed by one of us that when caesium nitrate is evaporated with strong nitric acid the last part of the acid is expelled with some difficulty, and the probable existence of a rather stable acid nitrate suggested itself. Mr. A. P. Beardsley, of this laboratory, undertook an examination of the matter last year, and upon dissolving caesium nitrate in hot nitric acid of sp. gr. 1.42 and cooling, obtained beautifully crystallized crops of the salt $HNO_3.CsNO_3$. The circumstances were such that Mr. Beardsley's work in this direction was interrupted, and we have undertaken a further examination of the subject.

Ditte[1] has described the following list of acid nitrates: $KNO_3.2HNO_3$, $NH_4NO_3.HNO_3$, $NH_4NO_3.2HNO_3$, $[2RbNO_3.5HNO_3]$, $[TlNO_3.3HNO_3]$.

The two formulæ enclosed in brackets do not correspond to the others or to the caesium salt mentioned above, and we have found that they are incorrect. In making these alleged compounds, $2RbNO_3.5HNO_3$ and $TlNO_3.3HNO_3$, Ditte saturated "monohydrated" nitric acid (the liquid corresponding to the formula HNO_3) with the normal nitrates and then simply analyzed the solution. He had prepared the other acid nitrates in the same way, but in these cases, having performed the operation above their melting-points, he was able to make definite compounds, and showed that the solutions became solid at definite temperatures.

We have easily succeeded in crystallizing two caesium and two rubidium acid nitrates, and a single thallium salt, and find that the salts of the last two metals do not correspond to the formulæ given by Ditte.

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[1] Ann. chim. phys., [5], 18, 320 (1878).

We have confirmed the composition of his potassium acid nitrate, and since his ammonium salts correspond exactly to the caesium and rubidium compounds, we assume that they are correct. Our revision and additions lead to the following list of acid nitrates:

	$KNO_3.2HNO_3$
$NH_4NO_3.HNO_3$	$NH_4NO_3.2HNO_3$
$RbNO_3.HNO_3$	$RbNO_3.2HNO_3$
$CsNO_3.HNO_3$	$CsNO_3.2HNO_3$
	$TlNO_3.2HNO_3$

These salts belong to two types, of which the diacid form is evidently most readily produced, since thallium and potassium apparently do not yield the other. The caesium salts are more easily prepared and are more stable than the others.

It has been supposed that "monobasic" acids are incapable of forming acid salts, and it is evident that this belief prevails at the present time, for the following statement is made in a recent text-book: "Acids like hydrochloric and nitric acids have not the power to form acid salts. They are called *monobasic acids*." This statement seems to be too sweeping, for there are many acid chlorides, some of which are well known and remarkably stable; in fact, their stability when in solution apparently leads to the opinion that they are not real acid salts. The following list will serve as examples of these compounds: $2HCl.PtCl_4$; $HCl.AuCl_3$; $2HCl.SnCl_4$; $HCl.ZnCl_2.2H_2O$; $2HCl.CuCl$; $2HCl.CuCl_2$; $5HCl.SbCl_5.10H_2O$. Iodides and bromides are also known, for example, $2HBr.SnBr_4$ and $HI.AgI$. The ease with which hydrofluoric acid forms acid salts is remarkable, and many acid salts of univalent organic acids, such as acetic, propionic, and valerianic acids are well known. Since it is now shown that the acid nitrates are well defined and in some cases comparatively stable bodies, the old idea that only "polybasic" acids are capable of forming acid salts should be entirely abandoned. The circumstance that acid nitrates are not more numerous is doubtless connected with the fact that double nitrates in general are rare.

Method of Preparation.—The monoacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ are readily prepared by saturating nitric acid of sp. gr. 1.42 with the normal nitrates at a gentle heat and cooling to crystallization. The use of a freezing-mixture, such as ice and salt, is desirable in making the rubidium compound, but it is not necessary for the caesium salt. Only normal potassium nitrate and thallous nitrate could be crystallized from nitric acid of this strength.

The diacid salts $KNO_3.2HNO_3$, $RbNO_3.2HNO_3$, $CsNO_3.2HNO_3$, and $TlNO_3.2HNO_3$ were all prepared by dissolving the normal nitrates to saturation in nitric acid of sp. gr. 1.50, and cooling with a freezing-mixture usually to considerably below 0°. In preparing the thallous compound, warming must be avoided because it causes the oxidation of a part of the thallium to thallic nitrate. When this has happened we find that the addition of alcohol, after the removal of most of the strong nitric acid by evaporation, is a convenient means of converting thallic nitrate into the thallous salt.

Properties.—The monacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ form large, flat masses of small, colorless, transparent crystals, apparently octahedra, arranged in parallel position. The diacid salts $RbNO_3.2HNO_3$ and $TlNO_3.2HNO_3$ form beautiful, colorless, transparent needles, while $CsNO_3.2HNO_3$ forms large, thin, colorless, transparent plates.

All the acid nitrates give off nitric acid more or less rapidly upon exposure to the air at ordinary temperature. The salt $TlNO_3.2HNO_3$ must be dried on paper in a very cool place, as its melting-point is below the ordinary temperature. The salt $RbNO_3.2HNO_3$ decomposes rapidly, and this also must be prepared for analysis in a cool place. The salt $RbNO_3.HNO_3$ and the two caesium salts are more stable than the others; the monacid salts are almost stable in the air, and may be preserved indefinitely in hermetically sealed tubes.

The melting-points of the acid nitrates as given by Ditte and found by ourselves are as follows:

$NH_4NO_3.HNO_3$	9° (Ditte)
$RbNO_3.HNO_3$	62°
$CsNO_3.HNO_3$	100°
$KNO_3.2HNO_3$	—3° (Ditte)
$TlNO_3.2HNO_3$	Undetermined
$NH_4NO_3.2HNO_3$	18° (Ditte)
$RbNO_3.2HNO_3$	39° to 46°
$CsNO_3.2HNO_3$	32° to 36°

The melting-points of the rubidium and caesium monacid nitrates are sharp, but the corresponding diacid salts melt gradually, evidently on account of decomposition. The salt $TlNO_3.2HNO_3$ melts below the ordinary temperature, but its exact melting-point was not determined.

Analyses.—The acid nitrates are very easily analyzed. The amount of normal nitrate was determined by simple heating, and the amount of nitric acid by titration. The following analyses were made with separate crops of the different compounds:

Monacid Rubidium Nitrate, $HNO_3.RbNO_3$.

		Found.		
	Calculated.	I.	II.	III.
HNO_3	30.00	30.51	....	30.18
$RbNO_3$	70.00	....	70.43	....

Monacid Caesium Nitrate, $HNO_3.CsNO_3$.

		Found.			
	Calculated.	I.	II.	III.	IV.[1]
HNO_3	24.42	24.23	24.13	....	24.28
$CsNO_3$	75.58	....	....	76.48	75.52

Diacid Rubidium Nitrate, $2HNO_3.RbNO_3$.

		Found.		
	Calculated.	I.	II.	III.
HNO_3	46.15	45.79	....	....
$RbNO_3$	53.85	....	53.74	53.44

Diacid Caesium Nitrate, $CsNO_3.2HNO_3$.

		Found.		
	Calculated.	I.	II.	III.
HNO_3	39.25	39.23	39.86	....
$CsNO_3$	60.75	....	....	61.22

[1] Determinations by H. P. Beardsley.

Diacid Thallous Nitrate, $TlNO_3.2HNO_3$.

	Calculated.	Found.		
		I.	II.	III.
HNO_3	32.14	33.13	33.02	....
$TlNO_3$	67.86	....	....	67.00

APRIL, 1901.

LXXXIII.—INVESTIGATIONS ON DOUBLE NITRATES.

I. CAESIUM DOUBLE NITRATES.

BY H. L. WELLS AND H. P. BEARDSLEY.

Comparatively few double nitrates have been described, and it is a curious circumstance that most of these are compounds of metals of the rare-earth group, as follows:

$2KNO_3.Ce(NO_3)_3.2H_2O$
$2NH_4NO_3.Ce(NO_3)_3.4H_2O$
$2NH_4NO_3.La(NO_3)_3.4H_2O$
$2NH_4NO_3.Di(NO_3)_3.4H_2O$

$3Mg(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2Ce(HO_3)_3.24H_2O$
$3Co(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mg(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2La(NO_3)_3.36H_2O$
$3Zn(NO_3)_2.2Di(NO_3)_3.60H_2O$
$3Ni(NO_3)_2.2Di(NO_3)_3.36H_2O$
$3Co(NO_3)_2.2Di(NO_3)_3.48H_2O$

$2KNO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$
$2NH_4NO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$

In addition to the above, the only normal double nitrates that have been found mentioned in the literature are the following:[1]

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[1] There are known, however, certain easily fusible mixtures of nitrates, such as potassium and lead nitrates, and thallous and silver nitrates, but apparently these do not form definite, crystallized compounds.

$KNO_3.Au(NO_3)_3$
$2KNO_3.Tl(NO_3)_3.H_2O$
$2NH_4NO_3.HgNO_3.2\frac{1}{2}H_2O$
$NH_4NO_3.AgNO_3$
$KNO_3.AgNO_3$
$3KNO_3.AgNO_3(?)$

With the exception of the auric and thallic salts, these are all compounds of an alkaline nitrate with a univalent nitrate. It appears to be a singular fact that no double nitrates of alkaline and bivalent metals are known to exist.

Since caesium is known to form double salts with great facility, we have attempted to prepare double nitrates of this metal with several bivalent metals which generally form double salts very readily. For this purpose we selected lead nitrate, cobalt nitrate, and mercuric nitrate ; but after the most careful work we were unable in any case to obtain a definite crystallized product, except crops of the simple nitrates. In each case there was evidence of combination from the fact that solutions were obtained which were much too concentrated to hold in solution the caesium nitrate that was present, if it had been uncombined. We conclude, therefore, that double nitrates were formed in solution in these cases, but that they were so exceedingly soluble that they could not be crystallized.

It seemed desirable to determine whether trivalent nitrates, other than those of the rare-earth metals, are capable of forming double nitrates with caesium nitrate. For this purpose we selected ferric nitrate, and succeeded, although with some difficulty, in preparing a double nitrate.

Caesium Ferric Nitrate,
$CsNO_3.Fe(NO_3)_3.7H_2O$.

This salt is formed at a rather low temperature in very concentrated solutions containing nitric acid and nearly equal molecular proportions of the compound salts. It forms pale-yellow, deliquescent, prismatic crystals, which melt, not sharply, at 33° to 36°. The following analyses were made with separate crops :

	Calculated for $CsNO_3.Fe(NO_3)_3.7H_2O$.	Found. I.	II.	III.
$CsNO_3$	34.64	....	35.51	34.87
$Fe(NO_3)_3$	42.98	42.29	42.73	42.68
H_2O	22.38	....	....	22.92
N	9.94	....	....	9.54

2. CAESIUM BISMUTH NITRATE, $2Cs_3NO.Bi(NO_3)_3$.

BY G. S. JAMIESON.

As a continuation of the investigation just described, experiments have been conducted with caesium nitrate and bismuth nitrate. The two salts were dissolved in widely varying proportions in dilute nitric acid, and the solutions were evaporated until crystallization took place on cooling. When 2.5 or more molecules of caesium nitrate to 1 molecule of bismuth nitrate were present, the simple caesium salt crystallized out; on the other hand, when the ratio of caesium to bismuth was less than about 1.5 to 1, bismuth nitrate was obtained. Between these limits a double salt was produced, particularly upon agitating the cold solution, in the form of colorless, prismatic crystals, which are stable upon exposure. These were sometimes more than a centimeter in length. The salt melts at 102°. Two crops gave the following analyses:

	Calculated for $2CsNO_3.Bi(NO_3)_3$.	Found. I.	II.
$CsNO_3$	49.75	47.00	51.22
$Bi(NO_3)_3$	50.25	52.63	48.16

The analyses do not agree very satisfactorily with each other, or with the calculated numbers. This was doubtless due to the syrupy nature of the mother-liquors, which made the drying of the crystals by means of filter-paper a difficult matter. The appearance of the crystals, in being homogeneous and different from the separate nitrates, however, leaves no doubt that this is a definite double nitrate.

3. THALLOUS THALLIC NITRATE, $2TlNO_3.Tl(NO_3)_3$.

BY F. J. METZGER.

When thallous nitrate is dissolved in concentrated nitric acid (sp. gr. 1.50) by the aid of heat, a part of the salt is oxidized to thallic nitrate, and upon cooling the properly concentrated solution, large, colorless, transparent, prismatic crystals are formed. The salt is very stable in dry air, but blackens when exposed to moisture. It melts at 150°. Several crops, made under different conditions, were analyzed.

	Calculated for $2TlNO_3.Tl(NO_3)_3$.	Found. I.	II.	III.
$Tl(NO_3)_3$	42.30	43.12	43.13	....
Total Tl	66.37	65.30	65.53	65.30

The thallic nitrate was determined by titrating the iodine set free by the salt from potassium iodide solution. The total thallium was weighed as iodide.

Conclusions.—No evidence has been obtained that alkaline nitrates form crystallizable double nitrates with the nitrates of bivalent metals.

Several trivalent nitrates, other than those of the rare-earth metals, are capable of forming double nitrates.

April, 1901.

LXXXIV.—ON CAESIUM PERIODATE AND IODATE-PERIODATE.

By H. L. Wells.

The two salts to be described were obtained as the result of an attempt to make a thorough investigation of the caesium salts of periodic acid. In view of the well-known complexity of periodates in general, it was expected that a considerable number of caesium periodates would be found, and it was hoped that they might be of much theoretical interest. As a result, however, only normal caesium periodate, $CsIO_4$, was obtained when caesium carbonate was added in widely varying proportions to solutions of periodic acid. This was so disappointing that experiments upon the addition of periodic acid to caesium hydroxide solutions, which were originally planned, were not carried out.

Preparation of Periodic Acid.—The principles involved in the method used for this purpose are not new, but as some of the details may be of use to others, a brief description of the process is given: 12.7 grams of iodine are put into a 10 per cent solution of 60 grams of sodium hydroxide. The liquid is heated to boiling in a flask, and a rapid stream of chlorine gas is passed into the continually boiling solution until the large amount of precipitate suddenly formed begins to cause bumping, when the flame is instantly removed, and the stream of chlorine is continued until no further increase is observed in the white precipitate of the periodate, $H_3Na_2IO_6$. While the liquid is still warm the precipitate is collected on a Büchner funnel and then thoroughly washed with cold water. It is dried in a steam-bath. The yield is usually about 22 grams, or 80 per cent of the theoretical. The sodium periodate is suspended in a large volume of water, 3 molecules of silver nitrate in solution are added, the liquid is boiled, filtered hot, and the black precipitate of silver periodate, Ag_3IO_5, is washed thoroughly with water.[1] The black silver periodate, while still moist, is suspended in a small amount of water, and chlorine gas[2] is passed in persistently, with agitation, until the precipitate has become nearly white. The silver chloride is removed by filtration, the liquid is concentrated on the water-bath, then brought to crystallization over sulphuric acid. After being drained the beautiful crystals of periodic acid are ready for use.

Caesium Periodate, $CsIO_4$.—This salt crystallizes in white plates, and is rather sparingly soluble in cold water. It was formed upon adding small quantities of caesium carbonate to concentrated solutions of periodic acid, and also when larger quantities, up to an excess of caesium carbonate, were used. It can be recrystallized readily by dissolving in hot water and cooling. When a very large excess of caesium carbonate was added to a solution of the salt and the mixture was evaporated to the point of crystallization more or less caesium iodate, $CsIO_3$, usually was formed on account of an accidental, or perhaps spontaneous, reduction, but no evidence of the existence of any other periodate was thus obtained. The following analyses of six separate crops were made, most of them for the purpose of identification :

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[1] The filtrate contains a considerable amount of periodate which is kept in solution by the nitric acid set free by the reaction. Most of this may be recovered in the form of the golden-yellow salt $H_3Ag_2IO_6$ by evaporating the liquid to very small volume and cooling, or after evaporating to dryness on the water-bath another crop of Ag_3IO_5 may be obtained by treatment with water.

[2] According to my experience chlorine is much better than bromine for this purpose.

	Calculated for $CsIO_4$.	Found. I.	II.	III.	IV.	V.	VI.
Cs	41.05	42.02	40.37	....	....	....	....
I	39.20	....	38.19	....	....	....	....
O	19.75	19.62	19.77	19.61	19.45	19.65	19.20

Caesium was determined by treating the substance with concentrated sulphuric acid, evaporating, converting into normal sulphate by ignition in air containing ammonia, and weighing. Iodine was determined as silver iodide after reduction with sulphurous acid solution. Oxygen was determined by titrating with sodium thiosulphate the iodine set free by the substance in a solution of potassium iodide in the presence of an acid.

Acid Caesium Iodate-Periodate, $HCsIO_3IO_4.2H_2O$.—This curious salt was first noticed as having crystallized after spontaneous evaporation from a solution of caesium periodate in dilute periodic acid, in which the periodate had suffered partial reduction. A second crop was purposely prepared from a similar solution, and a third product was made by dissolving caesium iodate and periodate in dilute periodic acid and cooling. It forms beautiful, slender, white prisms. The three crops gave the following results upon analysis :

	Calculated for $HCsI_2O_7.2H_2O$.	Found. I.	II.	III.
H	0.19	....	....	....
Cs	24.80	....	24.00	....
I	47.39	....	47.38	47.11
O	20.90	20.75	20.58	....
H_2O	6.72	....	....	....
	100.00			
Iodine as I_2O_5	23.69	....	....	23.20
" " I_2O_7	23.69	....	....	23.91

Iodic acid was determined by dissolving the substance in dilute nitric acid, precipitating silver iodate by the addition of silver nitrate, and weighing the silver iodide resulting from its ignition. The periodic acid left in the filtrate from the silver iodate was reduced by the addition of sulphurous acid, and the iodine was determined as silver iodide.

APRIL, 1901.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XIX.—CAMPHORIC ACID.

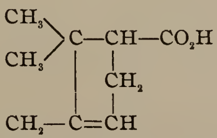
[TENTH PAPER.]

RACEMIC CAMPHOLYTIC ACID AND RACEMIC DIHYDROHYDROXYCAMPHOLYTIC ACID.

BY WILLIAM A. NOYES AND W. M. BLANCHARD.

A general concensus of opinion with regard to the structure of β-campholytic acid[1] appears to have been reached, and the work of Blanc, together with the synthesis of the 2-3,3-trimethylcyclopentanone effected in this laboratory, seem to place that structure beyond reasonable question.

Several of the chemists referred to have also adopted Bredt's formula for camphoric acid, and the following formula for α-campholytic acid:



We will not now enter into a full discussion of this formula, but will remark, in passing, that the evidence for the formula rests chiefly on the oxidation-products of the acid. It seems possible that these oxidation-products are abnormal, just as the oxidation-products of the β-campholytic acid are known to be. The trans formula discussed in our last paper furnishes a better explanation of almost all other facts with regard to the acid. In that paper[1] the opinion was expressed that Walker's inactive campholytic acid was the racemic form corresponding to the α-campholytic acid. We have now secured evidence which establishes the correctness of this view. The acid required for the investigation was prepared by allowing β-campholytic acid to stand in contact with fuming hydrobromic acid for several days, and by decomposing the resulting hydrobromide with caustic potash or caustic soda. As Walker supposed,[2] but did not fully prove, the hydrobromide of the β-campholytic acid at first formed gradually passes over, almost completely, into the hydrobromide of the α-acid. If we adopt the trans formula for α-campholytic acid the change takes place thus :

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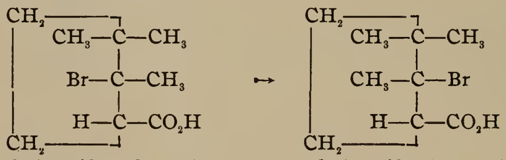
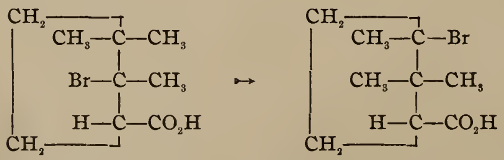
[1] Bredt, Lapworth, Blanc, Kerschbaum and Tigges, Walker, Perkin, and Forster have all expressed themselves, recently, as considering the acid to be Δ^{1}2,33-trimethylclycopentenecarboxylic acid. We adopt for the acid the designation proposed by Kerschbaum and Tigges (Ber. d. chem. Ges., **33**, 2936), as satisfactory. Forster's objection that the two campholytic acids are structurally different, even if it should prove that this is true, is not valid, since the α- and β-campholytic acids are, in any case, intimately connected, while there certainly is no close connection between β-campholytic acid and lauronolic acid. As Blanc and Bredt have also expressed themselves in favor of the nomenclature proposed, it is to be hoped that it may soon meet with general approval and that the name isolauronolic acid may be dropped.



Hydrobromide of β-campholytic acid. Hydrobromide of α-campholytic acid.

Such a transformation is in accord with the changes which are usual in stereomeric bodies and requires no special explanation. Bredt's formula, on the other hand, requires the following change :



Hydrobromide of β-campholytic acid. Hydrobromide of α-campholytic acid.

A transfer of the methyl group in the opposite direction must, of course, be supposed in the conversion of α-campholytic acid and of dihydrohydroxycampholytic acid into β-campholytic acid. While such transformations find their analogy, as Blanc[1] has pointed out, in the transformation of pinacone to pinacoline and *vice versa*, the explanation seems less probable than that given by ourselves. It was shown in the last paper that the hydrobromide of the active α-campholytic acid has not only the structure but also the exact configuration corresponding to the dihydrohydroxycampholytic acid. The significance of this fact seems to have been overlooked by Bredt, Forster, and others in their discussion. The trans formula explains it satisfactorily[2] while no other formula thus far proposed does so.

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[1] This JOURNAL, 24, 286.

[2] J. Chem. Soc., 77, 378.

When the hydrobromide of the racemic α-campholytic acid is treated with caustic soda there is formed, in addition to the regeneration of the campholytic acid, a small amount of the lactone first discovered by Kerschbaum and Tigges[3] and afterwards prepared by Blanc[4] and by Bredt,[5] and, in our experience, a small but, relatively, larger amount of a new hydroxy acid, which we have proved to be the racemic form of the well-known dihydrohydroxycampholytic acid, by separating it into its optically active components and identifying the right-handed form with that acid. As this new hydroxy acid undoubtedly corresponds in configuration to the hydrobromide of the racemic α-campholytic acid, and as that hydrobromide is always formed by the addition of hydrobromic acid to the racemic acid, it follows that that addition produces but *one* configuration (in a racemic form, of course) instead of the *two* configurations which an acid having Bredt's formula would give. The trans formula again gives a satisfactory explanation of these facts, while no other formula proposed does so.

The formation, in small amount, of a lactone on treating dihydroaminocampholytic acid with nitrous acid, leads Kerschbaum and Tigges, and Bredt to the conclusion that the amino group in that acid is in the γ position with regard to the carboxyl. This conclusion loses a part of its force from the following considerations: Camphoric acid, dihydroaminocampholytic acid, dihydrohydroxycampholytic acid, and the hydrobromide of α-campholytic acid are all active.

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[1] Compt. rend., **131**, 803.

[2] This JOURNAL, **24**, 289.

[3] Ber. d. chem. Ges., **33**, 2938.

[4] Bull. soc. chim., **23**, 81.

[5] Ann. Chem. (Liebig), **314**, 392.

For camphoric acid	$[\alpha]_{\mathrm{D}} = +47.2^\circ$
" dihydroaminocampholytic acid	$[\alpha]_{\mathrm{D}} = +53.7^\circ$
" dihydrohydroxycampholytic acid	$[\alpha]_{\mathrm{D}} = +72^\circ$
" bromdihydrocampholytic acid	$[\alpha]_{\mathrm{D}} = +93^\circ$

There is every reason to believe that these bodies all have the same configuration, differing only in the successive replacement of the carboxyl group by the amino group, by hydroxyl and by bromine. The new lactone, on the other hand, is inactive and must have, at least, a different configuration. That it is not derived from the racemic form of dihydrohydroxycampholytic acid is proved by the fact that the latter melts at 176° (see below), while the hydroxy acid corresponding to the lactone melts at 121°. That this acid is a stereomeric form, as suggested by Kerschbaum and Tigges, is possible, but cannot be considered as proved.

Bredt states recently in a foot-note[1] that the nitroso derivative of the anhydride of dihydroaminocampholytic acid gives the lactone on warming with sodium hydroxide. While it may be true that a small amount of the lactone is formed in this way, we find that the chief products of the decomposition are active α-campholytic acid and the active dihydrohydroxycampholytic acid. The last two products and *not* the lactone evidently correspond in structure to the amino acid. Further, we find that the active dihydrohydroxycampholytic acid is not converted into a lactone by acetic anhydride.

By the reduction of the hydroiodide of the racemic α-campholytic acid we have prepared a new dihydro-α-campholytic acid. From this we have obtained the α-bromine derivative, and from this, by means of alcoholic potash, a new campholytic acid. The double union in this acid must be in the position

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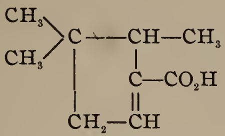
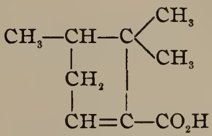
[1] Ann. Chem. (Liebig), 314, 392.

Δ^5 whether we accept the Perkin-Bouveault or Bredt's formula for camphoric acid.



Δ^5-Campholytic acid.
(Perkin-Bouveault.)



Δ^5-Campholytic acid.
(Bredt.)

The latter of these formulae has been recently proposed for α-campholytic acid by Forster. As the new acid is different from either α-campholytic acid or Forster's infracampholenic acid neither of these acids can have the structure represented by the second formula. An acid of either formula could be separated into optically active forms, but stereomeric forms are, otherwise, impossible.

EXPERIMENTAL PART.

The racemic α-campholytic acid was prepared by the method of Walker and Cormack.[1] Twenty grams of β-campholytic acid were placed in a Drechsel wash-bottle, 40 cc. of hydrobromic acid added, and a slow stream of hydrobromic acid gas was passed into the mixture for several days. The hydrobromide was then dissolved in ligroin and the solution shaken with a 10 per cent solution of caustic soda, the ligroin being shaken alternately with the hydrobromide and with the caustic soda till all of the hydrobromide had dissolved. On acidifying the alkaline solution and adding ligroin, the campholytic acid dissolves, while a portion of the racemic hydroxy acid remains undissolved and can be separated at once. A portion of the hydroxy acid remains in the aqueous solution and can be extracted with ether. Approximately 15 per cent of the hydrobromide is converted into the hydroxy acid.

The Racemic α-Campholytic Acid, $C_8H_{13}CO_2H$, boils at 127° to 128° under a pressure of 14 mm. It has heretofore been described as an oil, but one especially pure specimen crystallized in a cold room, and the crystals melted at 31°. An attempt to separate the acid into its components by means of the cinchonine and strychnine salts met with only a partial success, because of the unsatisfactory character of the salts. In one case an acid giving a slight rotation was obtained, but not in sufficient quantity or purity to determine the specific rotation.

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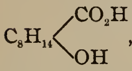
[1] J. Chem. Soc., 77, 380.

The Racemic Dihydrohydroxy Campholytic Acid,


$C_8H_{14}\begin{cases}CO_2H\\OH\end{cases}$

, prepared as described above, crystallizes from acetic ether or from water in needles which melt at 176°. The acid is stable toward permanganate. When warmed with dilute sulphuric acid it is converted into β-campholytic acid, melting at 132°.

I. 0.2012 gram substance gave 0.4612 gram CO_2 and 0.1680 gram H_2O.

II. 0.1561 gram substance gave 0.3586 gram CO_2 and 0.1312 gram H_2O.

	Calculated for $C_9H_{16}O_3$.	Found. I.	Found. II.
C	62.70	62.50	62.64
H	9.30	9.27	9.33

The hydroxy acid may also be prepared directly from the racemic α-campholytic acid by shaking it for a few minutes with fuming hydrobromic acid and treating the hydrobromide formed with caustic soda as before. This, together with the relation which was established in the last paper between the active α-campholytic acid, active hydroxy acid and active hydrobromide, leaves no doubt that the campholytic acid under discussion is in reality the racemic form corresponding to the active α-campholytic acid. That the hydrobromides of the active and racemic acids melt at the same temperature, is due to the fact that both melt with decomposition. The temperature of decomposition would be the same for an active as for the racemic form, while true melting-points are usually different, as is the case with the hydroxy acids.

Separation of the Racemic Dihydrohydroxycampholytic Acid into Its Components.

After several ineffectual attempts, the following method of separating the racemic hydroxy acid was successful. Molecular equivalents of the acid and of strychnine were put into a flask with 100 cc. of water for each gram of strychnine, and the mixture was heated for twenty-four hours on a water-bath. The solution was then filtered and allowed to evaporate spontaneously. When the solution was reduced to about one-fifth of its original volume, a number of fine, needle-like crystals were obtained. On further evaporation a new crop of crystals was formed and the process was continued till the solution was carried to dryness. The hydroxy acid was recovered from the various portions of the salt, and that from the first two portions was found to consist of a mixture of the inactive acid with the dextro acid, while the later portions consisted of the inactive acid with the laevo acid. By fractional crystallization, the inactive acid was removed from each, and there were finally obtained two portions, each melting at 132°, and one right-handed, the other left-handed, in its action on polarized light. When the dextro acid was mixed with some of the dextro acid prepared from dihydroaminocampholytic[1] acid, the melting-point was not changed. But when a portion of the laevo acid was mixed with some of the dextro acid prepared from the amino acid, the melting-point rose to 176°. A mixture of the two acids obtained from the inactive hydroxy acid also melted at 176°. This melting-point test with mixtures, because it can be so easily applied to small quantities of the acids, was extremely useful in following the course of the separation.

Owing to the difficulties of the separation, the rotation was determined with small amounts of the acids and with portions which were not quite pure.

I. 0.0765 gram of the dextro acid in 10 cc. of water gave a rotation of +0°.87 in a tube 188.6 mm. long.

II. 0.0908 gram of the laevo acid in 10 cc. of water gave a rotation of —1°.1 in the same tube.

This gives for the dextro acid $[\alpha]_D = +62°.3$ and for the laevo acid $[\alpha]_D = -64°.3$. The value for the pure dextro acid is +72°.

In the work just described β-campholytic acid has, for the first time, been connected with an active derivative of camphoric acid. The significance of the relation established has already been discussed.

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[1] This JOURNAL, 17, 424.

Amide of the Racemic α^1-Campholytic Acid.—This was prepared by treating the acid successively with phosphorus pentachloride and ammonia. Blanc[1] gives the melting-point as 103°. We found it a little lower, but did not purify the amide very carefully. The amide was prepared for comparison with the amide of Forster's infracampholenic acid, a sample of which Professor Forster very kindly sent us. The two are different. The amide of infracampholenic acid crystallizes in needles, this amide in leaflets, and the melting-points differ by 13°. A mixture of the two amides melts at a lower temperature than either.

Racemic α-campholytic acid differs from infracampholenic acid, also, in its conduct toward bromine. The latter gives a tribromdihydroinfracampholenic acid,[2] while the campholytic acid gave us, under the same conditions, in a solution in carbon disulphide, a mixture of dibrom-α-campholytic acid melting at 109° and dibrom-β-campholytic acid melting at 141°. The former gave, on analysis, 51.33 per cent of bromine, the latter 51.13 per cent. Theory requires 50.95 per cent.

Racemic Dihydro-α-Campholytic Acid, $C_8H_{15}CO_2H$.—Many unsuccessful attempts have been made, in this laboratory, in the endeavor to reduce the α-campholytic acid. The inactive acid has finally been reduced as follows: The hydroiodide of *i*-α-campholytic acid was prepared by passing hydriodic acid into a solution of the acid in ligroin.[3] The hydroiodide was then dissolved in cold alcohol and reduced by means of zinc dust. After separating the acids which resulted, they were dissolved in a solution of sodium carbonate and a solution of potassium permanganate added as long as it was decolorized. Acid sodium sulphite and sulphuric acid were then added in excess and the new acid was distilled over with water vapor. The acid was then taken up with ether, dried, and analyzed. As the analysis indicated that the acid was not quite pure, what remained was distilled. It showed a small amount of iodine vapors, on distillation, and was, accordingly, boiled with zinc and dilute sulphuric acid and distilled once more with steam. After drying, the acid was analyzed again and gave correct results. (Analysis II, below.)

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[1] Bull. soc. chim., **25**, 73.

[2] J. Chem. Soc. (London), **79**, 114.

[3] Blanc: Bull. soc. chim., **23**, 81.

I. 0.1788 gram substance gave 0.4488 gram CO_2 and 0.1610 gram H_2O.

II. 0.1975 gram substance gave 0.4998 gram CO_2 and 0.1815 gram H_2O.

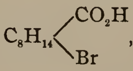
	Calculated for $C_8H_{15}CO_2H$.	Found.	
		I.	II.
C	69.23	68.45	69.02
H	10.25	10.00	10.21

Dihydro-α-campholytic acid boils at 245° to 247°. The relation in the boiling-points of the other related acids is of special interest :

α-Campholytic acid boils at 240° to 243°.
Dihydro-α-campholytic acid boils at 245° to 247°.
β-Campholytic acid boils at 255° to 256°.
Dihydro-β-campholytic acid boils at 244°.

It will be seen that the addition of hydrogen to the α-acid raises its boiling-point. It seems possible that this unusual effect is connected with the peculiar structure of the acid.

The *amide* of dihydro-*i*-α-campholytic acid crystallizes in needles, which melt at 103° to 104°. Both amide and acid are stable toward permanganate.

The α-*Bromdihydro-i-α-campholytic acid*,  $C_8H_{14}\begin{cases}CO_2H\\Br\end{cases}$, was prepared by treating the acid with phosphorus pentachloride and warming the resulting chloride with the calculated amount of bromine in a sealed tube. The phosphorus oxychloride was decomposed with ice-water, the chloride of the brom acid was then decomposed by warming with glacial formic acid, and the resulting brom acid was crystallized from formic acid. It crystallizes in needles which melt at 148°. It is difficultly soluble in cold formic acid.

0.1113 gram acid gave 0.0898 gram AgBr.

	Calculated for $C_8H_{15}O_2Br$.	Found.
Br	34.04	34.33

Δ⁵-Campholytic Acid, $C_8H_{13}CO_2H$.—The remainder of the brom acid was treated with alcoholic potash and the acid which was formed was crystallized from ligroin, in which it is easily soluble. The new acid crystallizes in needles which melt at 90° to 91°. Curiously enough, this is almost exactly the melting-point of the tetrahydro neighboring xylic acid.[1] A mixture of the two acids, however, melts below 60°. The acid, in a sodium carbonate solution, decolorizes potassium permanganate instantly, proving that it does not contain a trimethylene grouping. The amide of Forster's infracampholenic acid also decolorizes permanganate and so can contain no trimethylene ring. The position of the double union must be Δ^5 for either Bredt's or Bouveault's formula for camphoric acid, as has been pointed out above.

The *Amide* of Δ^5-campholytic acid crystallizes from ligroin in leaflets or small plates which melt at 90°. This is also the melting-point of the amide of infracampholenic acid, but a mixture of the two melts below 75°. The two acids are, therefore, different.

On warming with dilute sulphuric acid Δ^5-campholytic acid is not converted into β-campholytic acid. In this respect it differs from both α-campholytic acid and infracampholenic acid.

As the dihydro-α-campholytic acid was prepared from a racemic acid, it must be inactive. The Δ^5-campholytic acid must also be inactive. An active dihydrocampholytic acid could, doubtless, be prepared from the active campholytic acid.

Only about a gram of the dihydro-acid has been prepared thus far and the Δ^5-acid was not obtained in sufficient quantity for analysis. Its method of formation and conduct leave no question as to its composition.

TERRE HAUTE, May 25, 1901.

Since writing the above, the dihydro-α-campholytic acid has been prepared in larger amount and the Δ^5-campholytic acid obtained by shaking the ester of the α-brom acid with a solution of barium hydroxide.[2] The acid was mixed with some of the α-hydroxy acid and was purified for the first analysis by distillation with water vapor, for the second analysis by distilling again, and for the third by neutralizing with ammonia and distilling a third time. The ammonium salt dissociates and passes over with the steam. The results show the progressive purification of the acid :

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[1] This JOURNAL, 22, 3.

[2] Shepherd and Noyes : This JOURNAL, 22, 263.

I. 0.1929 gram substance gave 0.4815 gram CO_2 and 0.1565 gram H_2O.

II. 0.1563 gram substance gave 0.3922 gram CO_2 and 0.1281 gram H_2O.

III. 0.1800 gram substance gave 0.4588 gram CO_2 and 0.1476 gram H_2O.

	Calculated for $C_9H_{14}O_2$.	Found. I.	II.	III.
C	70.13	68.10	68.49	69.46
H	9.09	9.02	9.10	9.11

The α-hydroxy acid has thus far been obtained only as an oil which would not solidify and which has not been analyzed. The oxidation of this acid to a ketone, by means of lead peroxide and sulphuric acid, promises to give positive evidence as to whether the Perkin-Bouveault or Bredt's formula for camphor is the true one.

Aschan[1] has recently furnished what he considers to be conclusive evidence in support of Bredt's formula, by proving that the camphane obtained by the reduction of two active bornyl iodides is inactive. The proof seems to be inconclusive, as it has not been shown that the borneol prepared from either of the bornyl iodides gives an active camphoric acid by oxidation. Each of Aschan's bornyl iodides was prepared from pinene, and Marsh and Stockdale[2] have shown that the borneol from pinene hydrochloride gives an inactive camphoric acid by oxidation. If the borneol from Aschan's bornyl iodide should also give an inactive camphoric acid, the inactivity of the camphane would furnish no evidence as to the structure of camphor. That the bornyl iodide was formed by the addition of hydriodic acid to an unsaturated compound, cannot be considered as proof that its activity is not dependent on the position of the iodine atom,[3] since Phillips and one of us[4] have shown that the addition of hydrobromic acid may produce an active compound identical with that obtained by the replacement of a hydroxyl group by bromine. While the formulæ which we have given may not be true, there seems to be no escape from the conclusion that the activity of the bromdihydrocampholytic acid must depend, in part, on the asymmetric carbon atom to which the bromine is attached.

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[1] Ann. Chem. (Liebig), **316**, 196.

[2] J. Chem. Soc., **57**, 964.

[3] See Aschan, *Loc. cit.*

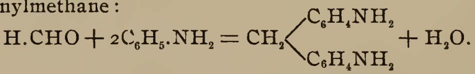
[4] This JOURNAL, **24**, 291.

TERRE HAUTE, July 1, 1901.

REVIEWS.

DER FORMALDEHYD. Seine Darstellung und Eigenschaften seine Anwendung in der Technik und Medicin. Bearbeitet von DR. L. VANINO unter Mitwirkung von DR. E. SEITTER. Wien. Pest. Leipzig: A. Hartleben's Verlag. 1901. Pp. 96 + vi.

In Germany alone 400,000 kilograms of formic aldehyde are manufactured yearly. Of this large quantity, 200,000 kilograms are used in the preparation of aniline dyes, and the rest in the tanning and paper industries and as a disinfectant. This pamphlet gives a great deal of information about formic aldehyde, and chemists will find it interesting and valuable. Formic aldehyde is sometimes called methyl aldehyde and, according to the new nomenclature, *methanal*. The commercial product, which is a water solution containing about 40 per cent of the aldehyde, is known as *formalin*. As is well known, the fundamental reaction that makes formic aldehyde of such importance in the aniline-dye industry, is that which takes place between the aldehyde and aniline, giving diamidodiphenylmethane:



$$H.CHO + 2C_6H_5.NH_2 = CH_2\left\langle\begin{matrix} C_6H_4NH_2 \\ C_6H_4NH_2 \end{matrix}\right. + H_2O.$$

When the product is mixed with aniline or with toluidine and the mixture oxidized, either pararosaniline or rosaniline is obtained.

A curious use of the aldehyde is in the preparation of fuming nitric acid. When the polymeric variety of the aldehyde, known as paraform, is added to nitric acid, nitrogen dioxide, NO, is evolved even in the cold. By heating gently and conducting the escaping gases into nitric acid, fuming nitric acid is obtained. Ludwig was the first one to make experiments on the use of formic aldehyde as a food preservative. He did not, however, sanction this use of it, as he held that the aldehyde would act injuriously on the human organism. This injurious action has been established by recent experiments of Bruns (Ann. di Farm, 1899, 324). The aldehyde has found extensive application in medicine; and as a disinfectant in cases of diphtheria, scarlet fever, measles, smallpox, tuberculosis, etc.

VOL. XXVI. OCTOBER, 1901. No. 4.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXXI.—SOME NEW DERIVATIVES OF SECONDARY BUTYL ALCOHOL.

BY JAMES F. NORRIS AND ERIK H. GREEN.

The source of the compounds which have been prepared was the so-called "oil of acetone" or "methylethyl ketone," which has recently been put upon the market as a commercial solvent. We were unable to find out from what substances the oil was prepared, but it is apparently identical with the French product described by Buisine,[1] which is made by the dry distillation of the calcium salts of the fatty acids obtained from wool-washings. The commercial oil contains about 60 per cent by volume of methylethyl ketone, which can be readily separated by fractionation. It seemed that the reduction of this ketone might offer a convenient method for obtaining secondary butyl alcohol, which has heretofore been prepared chiefly from its iodide, obtained by the action of hydriodic acid upon erythrite. We hoped to obtain the secondary alcohol in quantities sufficient for the preparation of the simple derivatives, of which very few are known, and for a study of the relations of the secondary butyl compounds to the isomeric normal, iso, and tertiary derivatives. As a large supply of the commercial oil was available, we made an extended study of the action of various reducing agents upon the ketone. No detailed comparative experiments on the reduction of fatty ketones have been reported in the literature, and it seemed of interest to determine under what conditions the reduction is most readily effected.

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[1] A. and P. Buisine: Compt. rend., **126**, 351.

The ketone was subjected to reducing agents in acid, neutral, and alkaline solution. The literature relating to the reduction of fatty ketones by acid agents is very scanty. The experiments of Bogdanowska[1] show that dibenzyl ketone is not reduced when treated with zinc and strong acids; the secondary alcohol was readily obtained, however, by the use of hydriodic acid and phosphorus. According to Bielohoubek,[1] methylpropyl ketone yields no alcohol on treatment with acid reducing agents; and, finally, Lachowitz[3] has shown that by the action of acids on iron or zinc the halogen can be easily removed from chlor ketones while the carbonyl group remains intact. On the other hand, the diketones, diacetyl (butadione), and acetylpropionyl (pentadione-2,3) yield ketols with zinc and dilute sulphuric acid; and, as Combs[4] has shown, acetylacetone (pentadione-2,4) is reduced to the corresponding glycol most readily by sodium amalgam in the presence of free hydrochloric or acetic acids. Further, it is well known that fatty aldehydes and aromatic ketones yield more or less readily to acid reducing agents. In view of these diverse results, we undertook a careful study of the action of acid reducing agents upon methylethyl ketone. Our results confirm those obtained by former workers on simple fatty ketones. All attempts to reduce the compound to secondary butyl alcohol by the action of hot or cold mineral and organic acids on zinc or iron were unsuccessful.

Attempts to reduce the ketone in neutral solution were also unsuccessful. Aluminum amalgam, which has been shown by Wislicenus[5] to be very efficient for the reduction of aromatic ketones, gave negative results ; no secondary alcohol could be obtained, though several experiments were made under varying conditions.

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[1] Ber. d. chem. Ges., **25**, 1272.

[2] *Ibid.*, **9**, 925.

[3] *Ibid.*, **17**, 1162.

[4] Ann. chim. phys., (6), **12**, 228.

[5] J. prakt. Chem., **54**, 46.

Reduction in alkaline solution was the only method which yielded the secondary alcohol. Sodium amalgam gave a yield of from 30 to 50 per cent of the theoretical quantity according to the conditions of treatment. The reduction required from one to two weeks for completion, and hence the process is inconvenient. As zinc and alcoholic potash gave excellent results as applied by Zagoumenny[1] to aromatic ketones, we attempted to reduce methylethyl ketone with this agent. Our results were unsatisfactory ; in one experiment no secondary alcohol was formed ; in another, under slightly different conditions, the yield was 4 per cent of the theoretical quantity. High-boiling condensation-products, doubtless analogous to those given by dibenzyl ketone,[2] were formed.

As it seemed probable that the action of aluminium and caustic soda upon the ketone might be analogous to that of sodium amalgam, we studied the effect of this reagent. Aluminium shavings were mixed with aqueous solutions of the ketone, and a concentrated solution of caustic soda then added gradually in small quantities. The alkali slowly threw the ketone out of solution, but, notwithstanding this fact, there resulted, in one experiment, a yield of 31 per cent of the theoretical quantity of secondary alcohol. When dilute alcohol was used as a solvent to keep the ketone in solution, no secondary alcohol was obtained, even after prolonged treatment with the reducing agent. The application of aluminium and caustic soda as a reducing agent will be further studied in this laboratory.

The action of sodium upon solutions of the ketone in methyl alcohol and in boiling amyl alcohol gave unsatisfactory results. Traces only of the secondary alcohol were formed, together with considerable quantities of high-boiling condensation-products.

Electrolytic hydrogen also gave poor results. The best yields were obtained with a current of from 1 to 2 amperes and half-normal caustic soda as the electrolyte, while the solutions were cooled by means of a water-jacket. Under these conditions 16 per cent of the theoretical yield of the secondary alcohol, with some dimethyl pinacone, were obtained in thirty-six hours.

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[1] Ann. Chem. (Liebig), 184, 175.

[2] Bogdanowska : Ber. d. chem. Ges., 25, 1272.

The action of sodium upon moist ethereal solutions of the ketone was found by far the most efficient process for reduction. We followed, in general, the method used by Rohn[1] for reducing methylisoamyl ketone, and by Wislicenus[2] for the reduction of methyl-β-butyl ketone. The ketone was dissolved in ether, floated over water in a flask attached to a reflux condenser, and reduced by the gradual addition of sodium in small chips. The process required from seven to eight days and gave a yield of about 50 per cent of the calculated quantity of secondary alcohol with about 15 per cent of dimethyl pinacone. When the ethereal solution was over a strong solution of sodium bicarbonate, as recommended by Bogdanowska,[3] in place of water, there was no increase in the yield of alcohol. When the reaction was carried out at the temperature of melting ice the yield of the secondary alcohol was increased to 74 per cent and the time required was reduced to four days.

The above results indicate that methylethyl ketone cannot be reduced to secondary butyl alcohol by acid or neutral agents. Alkaline reagents yield the alcohol in varying amounts up to 74 per cent of the calculated quantity. At high temperatures high-boiling condensation-products are formed ; at low temperatures the products are limited to secondary alcohol and dimethyl pinacone. The use of alcoholic solvents seems to be detrimental. Of the twelve agents studied, metallic sodium applied to a cooled, moist ethereal solution of the ketone was by far the most efficient.

The boiling-points of secondary butyl alcohol given in the literature, range from 96° to 100°, and the specific gravities at 0° from 0.827 to 0.850. Careful purification of our product with sodium, followed by repeated fractionation, resulted in a considerable quantity of the secondary alcohol boiling constantly at 99°.7 to 99°.9 (corr.) at 756 mm. pressure. This determination agrees very closely with that reported by Lieben,[1] who found the boiling-point to be 99° at 738 mm. The specific gravity of our preparation was 0.8078 at $\frac{20^\circ}{4^\circ}$, 0.8223 at $\frac{0^\circ}{4^\circ}$. Lieben gives the numbers 0.81 at 22°, 0.827 at 0°. The high values reported by other observers may perhaps be due to incomplete elimination of the halogen compounds involved in the preparation of the alcohol.

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[1] Ann. Chem. (Liebig), **190**, 309.

[2] *Ibid.*, **219**, 309.

[3] Ber. d. chem. Ges., **25**, 1272 .

As the secondary alcohol contains an asymmetric carbon atom, attempts were made to split the compound up into optically active substances by the action of various micro-organisms upon dilute solutions of varying strength at varying temperatures. In no case was an optically active substance obtained.

Secondary butyl chloride was readily obtained by passing dry hydrogen chloride through a boiling mixture of the secondary alcohol and zinc chloride, and by the action of phosphorus trichloride on the alcohol. The former method proved much more efficient than the latter. According to Malbot and Gentil[2] the use of zinc chloride is of no advantage in the preparation of the halides of higher homologues of ethyl alcohol. Our experiments, however, show that this statement does not hold good in the case of secondary butyl chloride; for when the zinc salt was omitted we could in no case get any secondary chloride by the action of hydrogen chloride at ordinary pressures. Estreicher,[3] however, whose paper appeared during the course of our work, obtained the halide by heating in sealed tubes solutions of hydrogen chloride in the secondary alcohol saturated at 0°.

Secondary butyl bromide, which was hitherto known[4] only in an impure state, we readily obtained in quantity by the action of phosphorus tribromide on the secondary alcohol. The alkyl bromide was not formed when dry hydrogen bromide was led through a boiling mixture of the secondary alcohol and zinc chloride, although by this treatment small amounts of the secondary chloride were obtained.

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[1] Ann. Chem. (Liebig), **150**, 114

[2] Ann. chim. phys., (6), **19**, 405.

[3] Ber. d. chem. Ges., **33**, 438.

[4] Meyer and Müller: J. prakt. Chem., **46**, 183.

Secondary butyl esters resulted from the action of acyl chlorides on the secondary alcohol. The acetic ester was the only one hitherto known. It is readily formed by the action of acetyl chloride and of a mixture of sulphuric and acetic acids upon the alcohol. The propionic and isovalerianic esters were prepared from the acid chlorides in an analogous way. Disecondary butyl succinic ester resulted when the secondary alcohol (1 mol.) was heated with succinyl chloride (1.2 mol.) although under these conditions the formation of the acid ester would be expected. The only products of the reaction were the neutral ester and succinic anhydride; the latter separated out in considerable quantity as the mixture cooled.

Attempts to obtain the benzoic ester by the Baumann-Schotten reaction resulted unsatisfactorily; and no ester was formed by leading dry hydrogen chloride through a boiling solution of benzoic acid in the secondary alcohol. It was readily obtained, however, by heating the alcohol with benzoyl chloride for some time.

By the fractionation of the high-boiling residue left from the rectification of the secondary butyl alcohol, we obtained the dimethyl pinacone (dimethyl-3,4-hexandiol-3,4) prepared by Lawrinowics[1] by the action of sodium amalgam upon methylethyl ketone. Zelinsky and Krapivin[2] consider this compound to exist in two stereoisomeric forms: a solid crystalline modification melting at 49°.5, and a liquid boiling at 200°–205°. They have found both forms to be of the same composition. The presence of two asymmetric carbon atoms is the basis of this view. Schram[3] has shown that both products have the same boiling-point. By repeated fractionation of our product we obtained the substance in a nearly pure state, boiling at 205° to 205°.7 (corr.). On cooling, white crystals separated which melted at 49°. Recrystallization from alcohol did not change the melting-point. A careful study of the properties of the crystals and the liquid from which they separated leads us to the view that the two products are not isomers but are the same substance. A mere trace of impurity probably prevents dimethyl pinacone from assuming the crystalline form. Liquid diisobutyl pinacone, as shown by Rohn,[1] crystallizes with great difficulty. Both the crystals and the liquid obtained by us were inactive to polarized light. Attempts to convert the dimethyl pinacone into dimethyl-3,4-dibrom-3,4-hexane, and to obtain subsequently from this a new octane were rendered futile by the difficulty of preparing the dibromide of the glycol in a pure state. No solid dibromide analogous to that obtained from ordinary pinacone by Pawlow[2] and by von Baeyer[3] could be isolated. Our product was an unstable oil which decomposed on distillation under reduced pressure.

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[1] Ann. Chem. (Liebig), **185**, 124.

[2] J. Chem. Soc. (London), **64**, 1, 390 (abstracts).

[3] Ber. d. chem. Ges., **16**, 1582.

By the action of sodium on secondary butyl bromide we obtained disecondarybutyl, one of the eighteen possible isomeric octanes, of which three were previously known: normal octane (b. p. 125°), diisobutyl (b. p. 109°), and hexamethylethane (b. p. 105° to 106°). Pure dry secondary butyl bromide is not affected by sodium even when boiled with the metal; a solution of the bromide in perfectly anhydrous ether was unaffected by standing over sodium for eight days. Reaction sets in, however, when the ether or the bromide is not wholly dry, as has already been shown by Silva[4] in the case of isopropyl bromide. Slight additions of ethyl acetate greatly hastened the reaction without, however, increasing the yield of octane. As is usual, a blue solid formed an intermediate product in the reaction. This decomposed when warmed gently, lost its color, and gave off disecondarybutyl. No hydrocarbon was formed until the blue compound was decomposed; and none was obtained by extracting the blue substance with ether. The composition and decomposition of this blue product will be further investigated. After distilling off the octane, the residual sodium still contained much organic matter, which accounts for the low yields of octane which were obtained. No gaseous products were evolved during the synthesis. Continued fractionation of the hydrocarbon failed to remove all of the halogen; even repeated distillation over sodium was ineffectual in this, although the octane had a nearly constant boiling-point. To get a halogen-free product, the crude octane resulting from a number of preparations was reduced first in a moist ethereal solution by sodium, then by the action of zinc on hydrochloric acid. The product, when washed with water and caustic potash, and fractionated, was completely free from halogen. About 0.5 gram, heated to 200° for two hours in a sealed tube with fuming nitric acid and silver nitrate, gave no indication of halogen.

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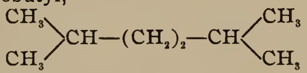
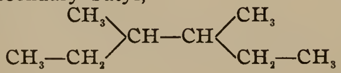
[1] Ann. Chem. (Liebig), **190**, 311.

[2] *Ibid.*, **196**, 124.

[3] Ber. d. chem. Ges., **26**, 2563.

[4] *Ibid.*, **5**, 948.

Disecondarybutyl boils at 116° to 116°.2 at 750 mm. pressure and has a specific gravity of 0.7332 at $\frac{0^\circ}{4^\circ}$. The high specific gravity of the substance is remarkable, for it is even higher than that of normal octane. This relation, however, is in agreement with that recently shown by Young and Fortey[1] to exist between diisopropyl and normal hexane. The following table shows the relation of disecondary butyl to its isomers, normal octane, and diisobutyl:

	B. p.	Sp. gr. at $\frac{0^\circ}{4^\circ}$.
Normal octane, $CH_3—CH_2—(CH_2)_4—CH_2—CH_3$	125°	0.7184
Diisobutyl,  $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH—(CH_2)_2—CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	109.°2	0.7102
Disecondary butyl,  $\left.\begin{matrix}CH_3\\CH_3—CH_2\end{matrix}\right\rangle CH—CH\left\langle\begin{matrix}CH_3\\CH_2—CH_3\end{matrix}\right.$	116°–116°.2	0.7332

A comparison of the constants of the simple secondary butyl derivatives above noted with the constants of the isomeric normal, iso, and tertiary butyl compounds, shows that the boiling-points of the secondary derivatives lie near to, but slightly lower than, the boiling-points of the isobutyl compounds; and with the exception of the alcohols and the succinic esters, the specific gravities in the two series bear the same relation. It would be expected, therefore, by analogy, that the boiling-point and specific gravity of disecondary butyl would be somewhat lower than the respective constants of diisobutyl. This, however, is not the case, for the relations are reversed, and disecondary butyl has the higher constants. It is interesting to note in this connection that propyl bromide has a greater specific gravity than has isopropyl bromide, yet dipropyl has a smaller specific gravity than has diisopropyl. The relations here are thus analogous to those existing between the isobutyl and secondary butyl derivatives. Further, it is interesting to note that the relations existing between the three octanes—normal octane, diisobutyl, and disecondary butyl,—as shown above, are precisely the same as regards both boiling-points and specific gravities as exist between the three isomeric decanes of analogous structure—normal decane, diisoamyl, and active diamyl, respectively.

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[1] J. Chem. Soc. (London), 77, 1127.

By the nitration of disecondary butyl with fuming nitric acid at 100°, a tertiary nitro compound was obtained in small quantity.

EXPERIMENTAL PART.

Reduction of Methylethyl Ketone.

The crude commercial oil was dried over potassium carbonate and fractionated by means of a tower 70 centimeters high filled with glass, as proposed by Hempel.[1] Five fractionations served to collect a large portion of the liquid in a fraction boiling at 79° to 82°; most of the residue boiled at 93° to 110°. The lower fraction had all the properties of methylethyl ketone; 750 cc. of the crude oil gave 420 cc. of the ketone, equivalent to 56 per cent by volume. The ketone was soluble in about 8 parts of water, readily soluble in dilute acids, but nearly insoluble in solutions of the alkali hydroxides. As there has been no systematic study of the reduction of a fatty ketone, we studied carefully the action of 12 reducing agents upon this ketone, and the results are given in some detail, as they are a contribution to laboratory practice which may prove of value.

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[1] Ztschr. anal. Chem., **20**, 502.

Reduction in Acid Solution.

Zinc and Glacial Acetic Acid.—The method of Krafft[1] for the reduction of higher fatty aldehydes was followed: 72 grams of the ketone, dissolved in 500 grams of glacial acetic acid, were boiled under a reflux condenser for a week with 225 grams of zinc dust—three and a half times the calculated quantity. Half the zinc was added at first, the remainder after three days. The product was made alkaline with caustic soda and shaken with ether. The ethereal solution, when dried over potassium carbonate and rectified, left a residue which boiled at 76° to 83°; it was unchanged ketone (b. p. 81°). Repetition gave a similar result.

Zinc and Dilute Sulphuric Acid.—Thirty grams of the ketone were dissolved in 300 cc. of water in a flask attached to an air condenser; 80 grams of zinc dust were added, and dilute sulphuric acid was poured in at intervals. The zinc sulphate formed gradually threw the ketone out of solution, and more water was added. After two days the zinc had almost all dissolved. The product was extracted with ether, and the extract dried over potassium carbonate and rectified. The residue, after removal of the ether, boiled at 76° to 83° and weighed 12 grams. It was unchanged ketone. No secondary alcohol was formed in the process. Other experiments resulted similarly. The great loss of ketone which occurred in this and also in the preceding experiment may possibly be due to complete reduction of the ketone to a hydrocarbon; for the work of Rötering and Zincke[2] on the reduction of ketonic acids to oxy-acids has shown that in this case there is often much loss due to the formation of hydro acids.

Iron and Acetic Acid.—Fifty grams of the ketone, dissolved in 360 grams of 50 per cent acetic acid, were heated gently on the water-bath under a reflux condenser with 77 grams of iron filings—twice the weight theoretically necessary. After twelve hours the semi-solid product was diluted, made alkaline, and extracted with ether as described above. No secondary alcohol was obtained; the ethereal extract contained only unchanged ketone. As in the previous methods, much ketone was lost. A check experiment gave similar results.

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[1] Ber. d. chem. Ges., **16**, 1715.

[2] *Ibid.*, **9**, 313.

Iron and Hydrochloric Acid.—Fifty grams of the ketone were dissolved in 300 cc. of water in a flask provided with an air-condenser and immersed in cold water. Seventy-seven grams of iron filings were added and then concentrated hydrochloric acid at intervals. The cooling was continued for twelve hours, and the reaction then allowed to progress at the room temperature for two days. The ethereal extract of the neutralized product was dried and fractionated. It yielded only unchanged ketone. The loss of ketone was about 50 per cent. Repetition gave a similar result.

Reduction in Neutral Solution.

Aluminium Amalgam.—The reagent was prepared as directed by Wislicenus and Kaufmann[1] and was freshly made for each experiment. Twenty-five grams, or twice the calculated quantity of aluminium amalgam, were added to a solution of 50 grams of the ketone in a liter of water in a flask attached to a reflux condenser. The mixture was agitated frequently. The evolution of hydrogen was vigorous. After forty-eight hours the liquid was decanted off, saturated with soda, and extracted with ether. The dried extract all distilled over below 89°, nearly all at 78° to 85° after removal of the ether. It was unchanged ketone. Repetition of the process with 50 grams of the amalgam and four days' treatment, gave essentially the same results.

Reduction in Alkaline Solution.

Sodium Amalgam (WITH B. R. RICKARDS).—Aqueous solutions of the ketone were treated in the usual way with 3 per cent sodium amalgam. Twice the calculated quantity of the amalgam was necessary, and the process was very slow.

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[1] Ber. d. chem. Ges., **28**, 1323.

Frequent agitation and neutralization of the alkaline liquid hastened the reaction. With frequent shaking by hand, the time required was from seven to ten days, and the yield of secondary alcohol was 30 per cent of the calculated amount. With mechanical stirring the yield rose to 50 per cent, but the time required was fifteen days. The alcohol was obtained from the product by fractionation of the ethereal extract, which had been dried over potassium carbonate. In all the experiments with sodium amalgam some dimethyl pinacone also was formed.

Zinc and Alcoholic Potash.—We followed the process recommended by Zagoumenny[1] for the reduction of benzophenone. Fifty grams of the methylethyl ketone in 200 grams of methyl alcohol were mixed with fifty grams of powdered caustic potash; 75 grams of zinc dust were added and the mixture heated on a water-bath under a reflux condenser. Methyl alcohol was used, as it could subsequently be separated easily from any secondary butyl alcohol. The heating was continued for five hours. The ethereal extract of the diluted product was dried over potassium carbonate and distilled. It all came over below 85°; the product was unchanged ketone. In another experiment 75 grams of caustic soda and 110 grams of zinc were used, and the heating was continued for ten hours. The result was much unchanged ketone, 3 grams of crude secondary butyl alcohol boiling at 90° to 115°, and a small quantity of a liquid boiling at 190° to 250°. The yield of the crude alcohol was 4 per cent of the theoretical quantity. The high-boiling liquid was not obtained in sufficient quantity for study, but it is doubtless a condensation-product analogous to those obtained by Bogdanowska,[2] when reducing dibenzyl ketone by this agent.

Aluminium and Caustic Soda.—Fifty grams of the ketone in 500 cc. of water were mixed with 25 grams—twice the calculated amount—of aluminium shavings in a flask provided with a reflux condenser. Concentrated caustic soda solution was added at intervals through the condenser tube. Hydrogen was evolved smoothly, and the action could be regulated by adding more or less alkali as the conditions required. As the mixture became more alkaline, the ketone separated partly from solution. After two days' treatment the oils were taken up with ether, dried, and fractionated. Sixteen grams of secondary butyl alcohol, boiling at 97° to 102°, and 27 grams of unchanged ketone were obtained, together with a small quantity of liquid which boiled above 102°. The yield of the secondary alcohol was 31 per cent of the theoretical amount. Experiments with dilute alcohol, as a solvent to prevent the separation of the ketone, resulted unsatisfactorily; no secondary alcohol was obtained by this treatment.

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[1] Ann. Chem. (Liebig), 184, 175.

[2] Ber. d. chem. Ges., 25, 1272.

Electrolytic Hydrogen (WITH B. R. RICKARDS).—A porous cup containing half-normal caustic soda as electrolyte was immersed in a 12 per cent aqueous solution of the ketone, which was kept cold by running water. The anode was of platinum, the cathode of iron gauze. With a current of 1 to 2 amperes the yield of secondary alcohol, in thirty-six hours, reached 16 per cent of the theoretical amount. Other experiments, under varied conditions, resulted in lower yields. In all cases some dimethyl pinacone also was produced.

Sodium and Methyl Alcohol, and Boiling Amyl Alcohol.—Thirty-five grams of sodium were added in small quantities at intervals to 50 grams of the ketone dissolved in 275 grams of methyl alcohol. The reaction required three days for completion. The product was decomposed with ice-water and extracted with ether. The final products were methyl alcohol, unchanged ketone, and a small quantity of a liquid boiling above 250°. No secondary alcohol was obtained. Treatment of the ketone in boiling amyl alcohol with sodium according to Bamberger's[1] method, gave unsatisfactory results also. From 36 grams of the ketone were obtained a few drops only of secondary alcohol boiling at 92° to 110°; the main product was a viscid oil which boiled at 250° to 290°. It was not further studied.

Sodium and Moist Ether.—The best yields of secondary butyl alcohol were obtained by the following process: 72

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[1] Ber. d. chem. Ges., **22**, 944.

grams of the ketone were dissolved in five times the volume of ether and floated over a liter of water in a flask attached to a reflux condenser. The mixture was kept cool by immersion in ice-water, and was shaken frequently during the reduction so that the ethereal layer should remain moist. Through the condenser 138 grams of sodium, in small pieces, were thrown in, in small quantities at a time—slowly at first, then more quickly as the reaction became less violent. The addition of the sodium required four days. The ethereal layer was then removed, dried over potassium carbonate, and fractionated. The yields of secondary butyl alcohol boiling at 97° to 102° ranged from 69 to 74 per cent of the theoretical quantity. The yields of dimethyl pinacone ranged from 11 to 14 per cent. With less than the stated amount of sodium, some ketone remained unreduced. When cooling was dispensed with, the yield of the secondary alcohol fell to about 50 per cent, and the time necessary was increased to from seven to eight days. When the reduction was carried out with no shaking the yield of the alcohol decreased about 10 per cent. The use of a strong solution of sodium bicarbonate, as recommended by Bogdanowska,[1] in place of water resulted in the formation of from 50 to 55 per cent of the secondary alcohol and from 11 to 14 per cent of dimethyl pinacone. The use of bicarbonate with simultaneous cooling gave similar results; but trouble was caused in this case by the crystallization of the sodium carbonate, which rendered the mixture below the ether nearly solid and delayed the action of the metal. It was necessary to use enough ether so that there was a layer at least 2 cm. deep; otherwise there is some danger of explosions owing to the expulsion of particles of metal which ignite above the ethereal layer. In one experiment, when a small quantity only of ether was used, the reaction-mixture exploded with extreme violence on the second day of reduction.

Secondary Butyl Derivatives.

Secondary Butyl Alcohol.—The crude alcohol obtained above was fractionated under a tower. The greater portion boiled at 99° to 100°; this portion was now cooled to 0° and some clean sodium added to it. After several hours the metal was removed and the liquid again fractionated. The greater part formed a fraction which boiled at 99°.7 to 99°.9 (corr.) at 756 mm. pressure. The final distillation was made over a fragment of sodium. The specific gravity of the alcohol was 0.8078 at $\frac{20^\circ}{4^\circ}$; 0.8226 at $\frac{0^\circ}{4^\circ}$. The alcohol was soluble in 8 parts of water at 20°, readily soluble in dilute acids, but nearly insoluble in strong solutions of the alkali carbonates and hydroxides. Sodium has almost no action upon it at 0°, very slow action at 15°, but decomposes it vigorously at 60°. Concentrated sulphuric acid decomposes it with charring when the mixture is not well cooled. Concentrated nitric acid decomposes it explosively. With solid potash and carbon disulphide it gives a white crystalline compound doubtless analogous to potassium xanthate.

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[1] Ber. d. chem. Ges., **25**, 1272.

Attempts to Obtain Optically Active Modifications of Secondary Butyl Alcohol (WITH B. R. RICKARDS).—Varying strengths of solutions of the secondary alcohol were submitted to the action of the following organisms: *Bacillus coli communis*; Lactic acid bacillus (Claflin); *Penicillium glaucum*; *Bacillus megatherium*; *Bacillus Topfii*. The tubes containing the cultures were subjected to various temperatures for several days. In all cases the solutions remained clear, no gas was evolved, and no acid was formed. No optically active substances were obtained.

Secondary Butyl Chloride.—Small yields were obtained by the action of phosphorus trichloride on the alcohol: 20 grams of the alcohol were heated to boiling in a flask attached to a reflux condenser, and 18 grams of phosphorus trichloride were then added, drop by drop, through the condenser. The mixture was boiled for two and a half hours. A yellow crust, which was found to be phosphorus, separated during the heating. The mixture was distilled into cold water. A light oil separated; this was washed with water and soda, and dried over calcium chloride. The product boiled at 65° to 69° and weighed 10 grams, 40 per cent of the theoretical amount. Repetitions of the process gave lower yields. Heating for less than two and a half hours caused a decrease in the yields. When the trichloride and the alcohol, in the proportions given, were allowed to stand together for two days at the room temperature, the quantity of secondary chloride formed was 16 per cent. Much better yields were obtained by leading dry hydrogen chloride through a boiling mixture of the secondary alcohol and zinc chloride: 20 grams of the alcohol with 15 grams zinc chloride were treated with dry hydrogen chloride for two hours. The yield of secondary butyl chloride was 15 grams, 60 per cent of the calculated amount. The gaseous products of the reaction were led through bromine which, on subsequent treatment with soda, yielded 14 grams of crude β-butylene bromide. A repetition of the process resulted in a yield of 64 per cent of the alkyl halide and 12 grams of β-butylene bromide. When no zinc chloride was present, no secondary butyl chloride was formed even by prolonged exposure of the boiling alcohol to the hydrogen chloride.

That the low yield obtained by the use of phosphorus trichloride in the previous experiments was not due wholly to the dehydrating action of the reagent, is shown by the fact that from 20 grams of the secondary alcohol and 18 grams of phosphorus trichloride only 5 grams of β-butylene bromide were obtained by leading the gaseous products through bromine. The loss is due, doubtless, to the formation of complex phosphorus ethers.

The crude secondary butyl chloride was washed, dried, and fractionated. It boiled at 67°.3 to 67°.8 (corr.) at 767 mm. pressure, and had a specific gravity at $\frac{20^\circ}{4^\circ}$ of 0.8707. With cold alcoholic silver nitrate, a precipitate began to form almost immediately. With aluminium chloride it evolved hydrogen chloride and formed a red oil, which was decomposed at once by water.

Secondary Butyl Bromide (with H. G. Johnson).—Thirty-six grams of phosphorus tribromide were slowly dropped into 20 grams of secondary butyl alcohol contained in a flask attached to a reflux condenser. The alcohol soon became hot, and boiled gently. The mixture was boiled for two and a half hours. Crusts of phosphorus separated, as noted under the preceding preparation. Towards the end of the heating a small quantity of white crystals formed in the condenser-tube. These crystals decomposed on exposure to the air and turned yellow. They dissolved in water and alkalies, and the solutions contained phosphorus. The crystals melted when hot water was poured into the condenser-casing. They were doubtless crystals of phosphonium bromide. The reaction-product was distilled with cold water and the oil which separated was washed with soda until it had no longer an odor of phosphine; it was then extracted with ether, dried over calcium chloride, and fractioned. The crude halide boiled at 88° to 93° and, the yield was 35 grams, or 94 per cent of the theoretical quantity. The gaseous products evolved during the process were led through bromine and yielded 1.5 grams of β-butylene bromide. Other experiments gave yields of the secondary bromide ranging from 80 to 90 per cent. When the alcohol was added to the phosphorus trichloride, instead of the contrary procedure, the yield fell to 65 per cent. Less than two and a half hours' boiling resulted in low yields, as was also the case when less than one and a half times the theoretical quantity of phosphorus tribromide was used. One molecule of the alcohol heated with 1 molecule of the tribromide yielded only 39 per cent of the secondary bromide. No secondary bromide was formed when dry hydrogen bromide was led through a boiling mixture of the alcohol and zinc chloride. The hydrogen bromide for this experiment was prepared by the action of bromine upon commercial anthracene. The purified gas was led through a boiling mixture of the secondary alcohol and zinc chloride for several hours. On rectification a small amount of secondary butyl chloride was obtained but no secondary bromide.

Fractionation of the crude bromide obtained by the numerous preparations gave a heavy, colorless, fragrant liquid boiling at 91°.3 (corr.). It had the specific gravity of 1.2507 at $\frac{25^\circ}{4^\circ}$. Determinations of the bromine by Carius' method resulted thus:

I. 0.1530 gram substance gave 0.2090 gram AgBr.
II. 0.1773 gram substance gave 0.2419 gram AgBr.

	Calculated for C_4H_9Br.	Found. I.	II.
Br	58.39	58.12	58.05

Pure secondary butyl bromide does not react with sodium, even at the boiling-point of the halide. It gives an immediate heavy precipitate with cold alcoholic silver nitrate. Attempts to prepare secondary butyl cyanide by boiling the halide in alcoholic solution with potassium cyanide were unsuccessful.

Secondary Butyl Acetate.—Luynes[1] prepared this ester by reduction of erythrite to secondary butyl iodide, which, with silver acetate, gave the ester boiling at 111° to 113°. Lieben[2] found its specific gravity at 0° to be 0.892. We prepared the ester very readily by warming the secondary alcohol with a little more than the calculated quantity of acetyl chloride. The mixture was allowed to stand twelve hours, then poured into cold water. The light oil was washed with a solution of sodium carbonate and with water, taken up with ether, dried over calcium chloride, and fractionated. It boiled at 111°.5 to 112° (corr.) at 744 mm. pressure. The specific gravity at $\frac{25^\circ}{4^\circ}$ was 0.8648; at $\frac{0^\circ}{4^\circ}$ it was 0.8900. The ester was also formed when a mixture of sulphuric and acetic acids was added to the secondary alcohol. The yield was small, however, owing to decomposition of the alcohol by the sulphuric acid.

Secondary Butyl Propionate.—To 20 grams of the alcohol contained in a flask attached to a reflux condenser, 30 grams of propionyl chloride were slowly added. The mixture was then heated on a water-bath for one hour. The product was poured into cold water. The separated oily layer was washed with a solution of sodium carbonate, taken up with ether, dried over calcium chloride, and fractionated. The product was a fragrant liquid which boiled at 132° to 132°.5 (corr.), and had the specific gravity of 0.8657 at $\frac{20^\circ}{4^\circ}$. The yield of the ester (boiling-point 130° to 134°) was 28 grams, or 82 per cent of the theoretical amount. Analysis gave the following results:

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[1] Jsb. d. Chem., 1868, 501.

[2] Ann. Chem. (Liebig), **150**, 112.

0.3006 gram substance gave 0.7137 gram CO_2 and 0.2768 gram H_2O.

	Calculated for $C_7H_{14}O_2$.	Found.
C	64.61	64.75
H	10.77	10.23

Secondary Butyl Isovalerianate.—Five grams of the secondary alcohol were treated with 8 grams of isovaleryl chloride, as described in the previous section on the propionic ester. The isovalerianic ester boiled at 163° to 164° (corr.) at 752 mm. pressure. The yield was 8 grams, or 73 per cent of the calculated amount. The specific gravity of the ester at $\frac{20°}{4°}$ is 0.8482. Analysis gave the following results:

0.1876 gram substance gave 0.4693 gram CO_2 and 0.1893 gram H_2O.

	Calculated for $C_9H_{17}O_2$.	Found.
C	68.35	68.22
H	11.39	11.21

Disecondary Butyl Succinate.—Perkin[1] obtained the isomeric diisobutyl ester by saturating with hydrogen chloride a mixture of succinic acid and isobutyl alcohol and letting the mixture stand with occasional warming. We find the action of succinyl chloride upon the secondary alcohol to be smooth and to result in the formation of the neutral ester only, even when excess of the acyl chloride is present. Thus, 17 grams of the alcohol and 35 grams—one and two-tenths times the theoretical quantity required—of succinyl chloride were heated on a water-bath under a reflux condenser for an hour. On cooling, long silky needles crystallized out. They were washed quickly with ether and dried between filters. The crystals melted sharply at 120°; they were soluble in water and formed a strongly acid solution which gave the reaction of succinic acid. Analysis showed that the crystals were succinic anhydride. The liquid which had been decanted from the crystals was poured into cold water; the oily layer which separated was washed with a solution of sodium carbonate, taken up with ether, dried over calcium chloride, and fractionated.

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[1] J. Chem. Soc. (London), 45, 519.

The product was a fragrant liquid which boiled at 255°.5 to 256°.5 (corr.) at 750 mm. pressure. Its specific gravity at $\frac{20^\circ}{4^\circ}$ was 0.9735. Analysis gave the following results:

0.2117 gram substance gave 0.4884 gram CO_2 and 0.1802 gram H_2O.

	Calculated for $C_{12}H_{22}O_4$.	Found.
C	62.60	62.91
H	9.56	9.55

Secondary Butyl Benzoate.—Twenty grams of the secondary alcohol and 40 grams of benzoyl chloride were heated together for four hours under a reflux condenser on a water-bath; 1 cc. of concentrated caustic soda solution was added and the heating continued for two hours longer. After cooling, an excess of caustic soda was added and the mixture allowed to stand until it no longer smelled of benzoyl chloride. The oil which separated was washed, taken up with ether, dried over calcium chloride, and fractionated. The product was a fragrant, slightly brownish liquid which boiled at 234°.5 to 235°.5 (corr.) at 757 mm. pressure. The yield of the crude ester was 15 grams, or 66 per cent of the theoretical quantity. The specific gravity of the ester at $\frac{25^\circ}{4^\circ}$ was 0.9945. Analysis gave the following results:

0.2161 gram substance gave 0.5856 gram CO_2 and 0.1538 gram H_2O.

	Calculated for $C_{10}H_{13}O_2$.	Found.
C	74.15	73.90
H	7.86	7.90

Attempts to obtain the ester by the Baumann-Schotten reaction resulted unsatisfactorily; the only product was a minute quantity of a fragrant oil. Attempts to prepare the ester by the action of hydrogen chloride upon a solution of benzoic acid in the secondary alcohol were also futile. Twenty grams of benzoic acid were dissolved in 20 grams of hot secondary butyl alcohol in a flask attached to a reflux condenser, and dry hydrogen chloride was then passed through the boiling solution. In a short time the contents of the flask solidified to a crystalline mass. The solid dissolved in caustic soda and a light, insoluble layer floated upon the alkaline liquid. The light layer was found to be secondary butyl alcohol; the solution, on acidification, gave a precipitate of benzoic acid. No ester was formed; the process thus failed on account of the slight solubility of benzoic acid in the secondary alcohol saturated with hydrogen chloride.

Disecondarybutyl (*Dimethyl-3,4-hexane*).—To 40 grams of secondary butyl bromide, diluted with 50 cc. of ether which had been dried over sodium but still contained a trace of moisture, were added 20 grams of finely shaved sodium. Reaction set in slowly, and after twenty-four hours a heavy blue deposit had formed upon the metal. The reaction was continued until further additions of sodium no longer became colored. The ethereal liquid was decanted and the residue washed repeatedly with dry ether. The combined ethereal extracts were fractionated; they contained only a small quantity of secondary butyl bromide. The blue residue was now heated; it became colorless and yielded a liquid which distilled over. The distillate boiled at 116° to 117° when rectified. It was a fragrant, mobile liquid, lighter than water, and insoluble in concentrated acids and alkalies. The yield of crude octane from 40 grams of the halide was 6 grams, or 30 per cent of the theoretical quantity. The process was repeated many times under varying conditions to discover, if possible, the cause of the low yields. When both the bromide and the ether were perfectly anhydrous, no reaction occurred even when the mixture was boiled. In one experiment the bromide dissolved in dry ether remained in contact with sodium for eight days without change. The addition of 0.5 cc. of ethyl acetate to this mixture caused a vigorous action to set in within twenty minutes, and the reaction was completed in twelve hours. The yield of crude octane in this case was 25 per cent. When no ethyl acetate was applied, the reaction required from four to five days for completion. As no gaseous products were evolved during the reaction, the cause of the low yields was sought in the residual blue substance. Until this blue compound was decomposed, no hydrocarbon was formed. Krafft[1] has proposed that the blue substance, which is a usual product of the Wurtz-Fittig synthesis, is a sodium compound which yields the hydrocarbons on decomposition. We find the residual sodium, after the decomposition of the blue substance, still to contain much organic matter. This may account for the poor yields of the hydrocarbon. The composition and decomposition of this intermediate blue compound will be further investigated. From 200 grams of secondary butyl bromide were obtained, by many repetitions of the synthesis, 23 grams of crude disecondary butyl boiling at 110° to 117°. It was washed thoroughly with strong hydrochloric acid, caustic potash, and water, taken up with ether, dried, and fractionated. The product, although boiling nearly constantly, still contained traces of halogen, which were not removed even by repeated distillation over sodium. The halogen was finally removed by means of nascent hydrogen. The hydrocarbon was dissolved in moist ether and treated with sodium; water was added at intervals. The treatment was carried out under a reflux condenser and lasted four hours. The ethereal solution was then washed, mixed with a little concentrated hydrochloric acid, and treated with zinc; the evolution of hydrogen was kept up for twelve hours. The product was washed with caustic soda and with water, dried with calcium chloride and with sodium, and fractionated. The disecondary butyl was now completely free from halogen. Half a gram heated to 200° for two hours with fuming nitric acid and silver nitrate, in a sealed tube, gave no indication of halogen.

Disecondarybutyl is a colorless liquid of a strong odor, something like that of petroleum ether. It boils at 116° to 116°.2 (corr.) at 750 mm. pressure. Its specific gravity at $\frac{0^\circ}{4^\circ}$ is 0.7332; at $\frac{25^\circ}{4^\circ}$ it is 0.7165. Analyses resulted as follows:

I. 0.1292 gram substance gave 0.3995 gram CO_2 and 0.1801 gram H_2O.

II. 0.1281 gram substance gave 0.3953 gram CO_2 and 0.1780 gram H_2O.

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[1] Ber. d. chem. Ges., 21, 3181.

	Calculated for C_8H_{18}.	Found. I.	II.
C	84.21	84.33	84.16
H	15.79	15.50	15.44

Molecular weight determinations made by V. Meyer's method gave the following results :

	Calculated for C_8H_{18}.	Found. I.	II.
Mol. wt.	114	118.7	113.3

Attempts to prepare the hydrocarbon by the action of reduced silver upon the secondary bromide were futile ; 9 grams of the halide were boiled under a condenser for four hours with 10 grams of "molecular" silver. No silver halide was formed. The mixture was distilled off ; it all boiled at 88° to 93° and weighed nearly 9 grams. Hence it was unchanged secondary bromide upon which finely divided silver seems to have no action.

Nitration of Disecondarybutyl.—As Young and Francis[1] have shown that the isoparaffins, including diisobutyl, are readily nitrated when heated at 100° with fuming nitric acid, we studied the action of nitric acid upon disecondary butyl. Four grams of the hydrocarbon were heated with 25 grams of nitric acid, of sp. gr. 1.59, for two days on a water-bath under a reflux condenser. During the nitration much carbon dioxide was given off. The product, on dilution, yielded 0.5 gram of a fragrant, heavy, yellow oil, which gave a red color with caustic potash and was completely volatile with steam. It did not give the nitrolic acid or pseudonitrole reactions ; hence it was a tertiary nitro compound and thus differed from the nitro derivatives obtained by Worstall[2] from normal hydrocarbons. The number of nitro groups in the substance could not be determined, as the available quantity of the compound was insufficient for its purification and analysis.

Dimethyl Pinacone (*Dimethyl-3,4-hexandiol-3,4*).—The crude dimethyl pinacone obtained by rectification of the products of the reduction of the methylethyl ketone was fractionated repeatedly from a distillation flask, the neck of which was filled with glass beads, kept in place by a coil of platinum wire suspended from the cork. Several fractionations with this apparatus collected the greater part of the glycol in a fraction boiling at 203° to 205° (uncorr.). This, on further fractionation, yielded a product which boiled at 205° to 205°.7 (corr.) at 752 mm. pressure. Previous observers have reported the substance as boiling at 200° to 205°. The liquid, when cooled, solidified almost completely to a mass of white crystals, which melted at 49°. Zelinsky and Krapivin[1] found the melting-point to be 49°.5 when the crystals were recrystallized from ether. Recrystallization of our product from alcohol did not change the melting-point. When the crystals were not completely free from the original mother-liquor they melted at a much lower temperature. Schramm[2] has found that the crystals and liquid have the same boiling-point, and Zelinsky and Krapivin found the two to be of the same composition. Neither the crystals nor the liquid obtained by us were optically active. The two forms were identical as regards solubility in all ordinary solvents. The solubility of the substance was remarkable, as it dissolved in water and in all organic solvents; it was insoluble, however, in solutions of alkali hydroxides. No solid hydrate analogous to that formed by common pinacone could be obtained by the action of water. It seems probable that pure dimethyl pinacone is a crystalline solid which, when melted, is prevented from crystallizing by mere traces of impurities. Rohn[3] has shown that diisobutyl pinacone crystallizes with great difficulty after it has been melted. In confirmation of the view that the solid and liquid products are the same substance, is the fact that, during the fractionation of the substance, the fractions yielded crystals with greater readiness and in larger quantity as the boiling-point approached that of the pure substance. The specific gravity of the liquid dimethyl pinacone, boiling at 205° to 205°.7, was 0.9529 at $\frac{25^\circ}{4^\circ}$. Attempts to prepare dimethyl-3,4-dibrom-3,4-hexane by the action of dry hydrogen bromide on the dimethyl pinacone dissolved in glacial acetic acid, as proposed by Pawlow[1] for the preparation of the corresponding derivative of common pinacone, resulted unsatisfactorily. Ten grams of the glycol were dissolved in 100 grams of glacial acetic acid in a flask attached to a reflux condenser. Dry hydrogen bromide was then passed through the cooled solution for several hours. The solution turned a dark-purple color, but no crystals separated even after standing for a week. The liquid was made alkaline with caustic soda; a black oil separated and was taken up with ether, dried, and distilled at 100 mm. pressure. The oil decomposed and gave off hydrogen bromide in large quantity. Phosphorus tribromide reacts violently with the glycol; the product, after dilution, was a heavy oil. It was not further studied.

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[1] J. Chem. Soc. (London), 73, 928.

[2] This JOURNAL, 20, 202.

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[1] Abstract in J. Chem. Soc. (London), **64**, 390.

[2] Ber. d. chem. Ges., **16**, 1582.

[3] Ann. Chem. (Liebig), **190**, 311.

Action of Zinc and Hydrochloric Acid upon Dimethyl Pinacoline (Dimethyl-3-hexanon-4).—The action of acid reducing agents upon methylethyl ketone, as shown above, produced no secondary butyl alcohol but, nevertheless, resulted in a great loss of the ketone. If this loss were due to complete reduction of the ketone to gaseous butane the action of acid reducing agents upon dimethyl pinacoline,

$$CH_3.CH_2.C(CH_3)_2.CO.CH_2.CH_3,$$

should result in the formation of an octane. Such a result would explain the loss above mentioned. The dimethyl pinacoline was prepared as directed by Lawrinowics.[2] Five grams of dimethyl pinacone and 20 grams of 50 per cent sulphuric acid were heated together for two hours on a water-bath under a reflux condenser. The ethereal extract of the diluted product was dried and rectified. The crude dimethyl pinacoline boiling at 135° to 150° was then dissolved in ether and reduced by zinc and concentrated hydrochloric acid. The reduction extended over two days. The ethereal solution was then washed, dried over potassium carbonate, and fractionated. After removal of the ether nothing distilled over below 140°. Fraction 140°–165° weighed 2 grams; the remainder of the product boiled at 250° to 300° and weighed nearly 2 grams. Hence no octane was formed, for normal octane boils at 125° and hexamethyl ethane at 106°. The experiment therefore sheds no light upon the loss which methylethyl ketone suffers during reduction by acid reagents.

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[1] Ann. Chem. (Liebig), **196**, 124.

[2] *Ibid.*, **185**, 126.

Indices of Refraction of the Secondary Butyl Derivatives.— We are indebted to Prof. G. V. Wendell, of the Institute, for the measurements of the indices of refraction of the compounds noted below. The indices were determined for the sodium ray and with respect to air at 20°. The instrument used was the improved Pulfrich refractometer :

	n_D.	Temp.
Secondary butyl alcohol	1.3949	25°.30
Secondary butyl acetate	1.3866	25°.30
Secondary butyl propionate	1.3938	25°.19
Disecondary succinate	1,4238	25°.25
Secondary butyl chloride	1.3953	25°.20
Secondary butyl bromide	1.4344	25°.25
Dimethyl pinacone	1.4521	25°.25
Disecondarybutyl	1.4038	25°.20

BOSTON, May 5, 1901.

XXXII.—ON THE ISOMORPHISM OF SELENATES AND TELLURATES.

BY JAMES F. NORRIS AND WILLIAM A. KINGMAN.

The uncertainty about the position of tellurium in the periodic system of the elements has led to a number of investigations on the isomorphism of the compounds of tellurium with those of selenium on the one hand, and with those of the platinum metals on the other. Retgers[1] found that potassium tellurate was not isomorphous with potassium selenate, but was isomorphous with potassium osmate. From a study of tellurium and its compounds, he came to the conclusion that there existed no true case of isomorphism either between selenium and tellurium, or between the compounds of these elements. The apparent isomorphism of the selenides and tellurides was, according to him, due to the fact that these compounds crystallize in the cubic system, in which substances of widely different chemical properties form mixed crystals on account of the high crystallographic symmetry of the system. Retgers, therefore, proposed to place tellurium in the eighth group in the periodic system.

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[1] Ztschr. phys. Chem., 8, 70.

In a paper published some time ago by one of us,[1] it was shown that the salts of the composition $SeBr_4.2(CH_3)_2NH.HBr$ and $TeBr_4.2(CH_3)_2NH.HBr$ are isomorphous with one another but not with the platinum salt of analogous composition. These salts do not crystallize in the cubic system. The results showed that in this case, at least, the two elements are isomorphous. On account of this fact it seemed advisable to study more fully the isomorphism of the selenates and tellurates. The potassium salts alone have been studied and were found not to form mixed crystals. These salts have the composition $K_2TeO_4.2H_2O$ and K_2SeO_4. Potassium osmate, with which potassium tellurate is isomorphous, has the composition $K_2OsO_4.2H_2O$.

It seemed to us that the failure to form mixed crystals of potassium selenate and potassium tellurate might be due to the fact that one salt contained water of crystallization, while the other was anhydrous. We, accordingly, attempted to find two salts of selenic and telluric acids which either were anhydrous or contained the same number of molecules of water of crystallization. In this we were unsuccessful, but the results which have been obtained are of sufficient interest to warrant publication.

The ammonium and lithium salts of the two acids are described as anhydrous in the literature. The tellurates of these bases we found to be uncrystallizable gums, which, therefore, could not be used in the investigation. As no selenate has been described which has the same number of molecules of water as the analogous tellurate, we undertook the preparation of some new salts of these acids.

Cerium tellurate was first made. It seemed advisable to make this compound since cerium selenate crystallizes with three different quantities of water. Cerium carbonate was insoluble in telluric acid. When a solution of sodium tellurate was added to a solution of cerium sulphate, a white precipitate was formed, which was shown to be cerium tellurate.

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[1] This JOURNAL, **23**, 486.

As the cerium salts could not be used to study the isomorphism of the selenates and tellurates the rubidium and caesium salts were prepared. The neutral selenates of these metals have been made and carefully studied by Tutton.[1] The salts are anhydrous and isomorphous with the corresponding sulphates. Caesium tellurate was prepared and found to be a well crystallized compound. As the salt contained 3 molecules of water, the acid salts were next made, as the chances for the formation of anhydrous salts in this case were greater. There was also a difference in composition in these salts. The acid selenates of rubidium and caesium are very soluble, well-crystallized, anhydrous salts; the acid tellurates, on the other hand, are much less soluble, crystallize with difficulty, and contain 0.5 molecule of water of crystallization. Notwithstanding this difference, the isomorphism of the salts was investigated with the result that mixed crystals of the compounds could not be formed.

The question of the isomorphism of selenium and tellurium cannot be settled, it appears, by a study of salts of selenic and telluric acids. All of the tellurates except those of the alkali metals are insoluble, and the soluble salts do not resemble the analogous selenates in crystal form, solubility, or content of water of crystallization.

EXPERIMENTAL.

Rubidium Hydrogen Tellurate, $RbHTeO_4.\frac{1}{2}H_2O$.—This salt was made by mixing solutions of rubidium carbonate and telluric acid containing the theoretical quantities of the two substances for the acid salt: 1 gram of crystallized telluric acid and 0.5 gram rubidium carbonate were used. When the solution was concentrated by heat, an amorphous powder separated. On spontaneous evaporation a crystalline crust appeared. These two forms were analyzed for water and telluric acid.

In determining telluric acid, a solution of about 0.5 gram of salt in 50 cc. hydrochloric acid (sp. gr. 1.12) was boiled until the volume was reduced about two-thirds. The chlorine which was evolved was drawn, by means of a current of air, through a strong solution of potassium iodide, which was kept cold by ice-water. The liberated iodine was titrated with a solution of sodium thiosulphate. One atom of tellurium in the form of telluric acid liberates 2 atoms of chlorine. The determinations of tellurium were all made with the anhydrous salts which were dried to constant weight at 120°.

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[1] J. Chem. Soc., 71, 846.

The results of the analyses follow: Analysis I is of the amorphous powder and Analysis II is of the crystalline crust:

	Calculated for		Found.	
	$RbHTeO_4.\frac{1}{2}H_2O$.	$RbHTeO_4$.	I.	II.
H_2O	3.16	....	3.73	3.49
Te	....	44.44	44.82	44.91

The salt is soluble in about 20 parts of cold water, but slightly more soluble in hot water.

Caesium Hydrogen Tellurate, $CsHTeO_4.\frac{1}{2}H_2O$.—On evaporation of a solution containing 1 gram of caesium carbonate and 1.5 grams crystallized telluric acid and subsequent cooling, a white amorphous powder separated. Later a crystalline crust was formed, which appeared to consist of very small cubical crystals. The salt was less soluble than the corresponding rubidium salt. It required about 30 parts of water for its solution.

An analysis of the crystals resulted as follows:

	Calculated for		
	$CsHTeO_4.\frac{1}{2}H_2O$.	$CsHTeO_4$.	Found.
H_2O	3.96	....	4.19
Te	....	39.17	39.50

Rubidium Hydrogen Selenate, $RbHSeO_4$.—This salt was prepared by adding to a solution of rubidium carbonate twice the quantity of selenic acid required to neutralize it. The solution, on evaporation, yielded well-formed crystals which were soluble in about their own weight of water. The salt was very hygroscopic. It was shown to be anhydrous by heating to 120° a weighed quantity of the salt which had been dried over sulphuric acid. The selenium was determined in the following way: About 0.4 gram salt was dissolved in 25 cc. concentrated hydrochloric acid diluted to 100 cc. The solution was boiled for one hour, care being taken to keep the volume between 75 and 100 cc. The selenium in the resulting solution was precipitated by sodium hydrogen sulphite, dried, and weighed. The analysis resulted as follows:

	Calculated for $RbHSeO_4$.	Found.
Se	33.12	33.32

Caesium Hydrogen Selenate, $CsHSeO_4$.—This salt was prepared from caesium carbonate and selenic acid. The solution was evaporated nearly to dryness before crystals appeared. The salt crystallizes in large flat plates with pointed ends and is exceedingly hygroscopic. The compound was shown to have no water of crystallization. A selenium determination gave 28.63 per cent instead of 28.80 per cent, the theoretical amount.

Rubidium Tellurate, $Rb_2TeO_4.3H_2O$.—As rubidium tellurate is decomposed by carbon dioxide, the salt cannot be made from rubidium carbonate and telluric acid. It was prepared by neutralizing the acid with rubidium hydroxide. An excess of about 25 per cent of the base was added, and the solution was evaporated in a vacuum desiccator over sulphuric acid. The salt crystallizes in prisms terminated by pyramids, and is soluble in about 10 parts of water. The analysis resulted as follows:

	Calculated for $Rb_2TeO_4.3H_2O$.	Found.
H_2O	12.96	13.10
Te	35.29	34.74

Attempt to Form Mixed Crystals of the Acid Rubidium Salts of Selenic and Telluric Acids.—On account of the fact that there was but 0.5 molecule of water in rubidium hydrogen tellurate, we studied the isomorphism of this salt with rubidium hydrogen selenate. In working out an analytical method for the determination of a selenate in the presence of a tellurate, we studied a method of separation of selenium and tellurium. This method did not give results sufficiently accurate for it to be recommended for quantitative work, but it served to test the isomorphism of the compounds under investigation.

When telluric and selenic acids are boiled with strong hydrochloric acid, they are reduced to the lower state of oxidation. If to such a solution a strong solution of potassium iodide is added, the selenium is precipitated and the tellurium is converted into tellurium iodide, which remains in solution in the excess of potassium iodide. These reactions were tested quantitatively. 0.2436 gram rubidium hydrogen selenate was boiled for an hour with 25 cc. concentrated hydrochloric acid diluted to 100 cc., care being taken to keep the volume between 75 and 100 cc. After cooling, a saturated solution of potassium iodide was added in large excess. The precipitated selenium was washed by decantation with warm potassium iodide solution, then with water, and finally, after drying at 110°, was weighed. 0.0849 gram of selenium was obtained. This corresponds to 34.85 per cent instead of 34.42 per cent, the amount required by theory. This experiment showed that selenium could be determined in this way with a fair degree of accuracy.

The separation of selenium from tellurium was studied by treating a solution of selenium dioxide and tellurium dioxide in hydrochloric acid with potassium iodide, filtering, washing with potassium iodide, and weighing the selenium. In two experiments about 0.35 gram of tellurium dioxide was mixed with weighed quantities of selenium dioxide.

Gram SeO_2 used.	Gram Se used.	Gram Se found.
0.1521	0.1082	0.1101
0.2041	0.1452	0.1527

Although these results are far from accurate the method is so rapid and convenient that it was used. The results obtained were found sufficiently accurate for the purpose.

An aqueous solution of molecular quantities of the acid rubidium salts of selenic and telluric acids was allowed to evaporate spontaneously. The first two crops of crystals were analyzed in the manner described above. The selenium determinations gave the following results :

I. 0.3029 gram of first crop of crystals gave 0.0029 gram Se.

II. 0.3327 gram of second crop of crystals gave 0.0087 gram Se.

	Calculated for $RbHTeO_4.RbHSeO_4$.	Found.	
		I.	II.
Se	13.59	0.95	2.61

These results show that the two salts are not isomorphous.

BOSTON, May 6, 1901.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON GOLD HALIDES.

BY FELIX LENGFELD.

Though the gold halides have been extensively investigated by Thomsen,[1] Schottländer,[2] Krüss,[3] and others, the data given are frequently contradictory, and it therefore seemed that some results obtained in the course of an attempt to obtain silver salts of halauric acids might be of interest.

Aurous Chloride.

Aurous chloride is easily made by heating auric chloride to 175° for several days.[4] The decomposition of the auric salt is complete and the product is almost pure aurous chloride. For instance, one specimen contained 85.95 per cent gold and 14.06 per cent chlorine (calculated 84.76 per cent and 15.24 per cent). Below 175° auric salt is left, above 175° aurous chloride decomposes more easily. Aurous chloride is insoluble in water and dilute nitric acid. Concentrated nitric acid gradually decomposes it, auric salt going into solution leaving a residue of gold. On adding nitric acid to its ammoniacal solution a white curdy precipitate resembling silver chloride is formed. This could not be analyzed, as it decomposes when washed, forming auric salt and free gold. Aurous chloride dissolves in hydrochloric and hydrobromic acids and in the alkali chlorides and bromides with decomposition. With bromides the decomposition is more rapid than with chlorides. With a solution of potassium bromide it gives gold and a brownish-red liquid that contains no free bromine but potassium chloraurate and bromaurate,

$$4KBr + 12AuCl = KAuBr_4 + 3KAuCl_4 + 8Au.$$

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[1] J. prakt. Chem., (2), **13**, 337; Therm. Unters., **3**, 390, etc.

[2] Ann. Chem. (Liebig), **217**, 312.

[3] Ber. d. chem. Ges., **20**, 211, 2634; Ann. Chem. (Liebig), **238**, 241; etc.

[4] Fignier: J. Pharm., **6**, 84; **8**, 157. Thomsen: *Loc. cit.* Krüss: Ann. Chem. (Liebig), **237**, 276.

A solution of sodium chloride takes it up with little decomposition and is at first almost colorless. A double salt, perhaps $NaAuCl_2$, is formed. The double salt is unstable for, on standing, gold is deposited (often as an excellent mirror) the solution becomes yellow and contains the salt $NaAuCl_4$.

Aurous chloride is slowly decomposed by ether, alcohol, and acetone, auric chloride going into solution.

Aurous Bromide.

Aurous bromide may be obtained almost pure by heating bromauric acid on the water-bath three hours and then to 105° for twelve hours.[1] No auric salt is left, but usually a little gold is set free. Analysis showed 72.68 per cent gold and 27.09 per cent bromine (calculated 71.14 and 28.86 per cent). The substance is gray, amorphous, and resembles the chloride. It is insoluble in water, nitric or sulphuric acid, is slowly decomposed by alcohol, ether, acetone, and moist chloroform, and dissolves with partial decomposition in ammonia. Nitric acid, added to its ammoniacal solution, gives an unstable precipitate partly soluble in ammonia, so that after several repetitions of the operation all the salt is decomposed. Potassium cyanide dissolves the salt without decomposition. Potassium bromide gives potassium bromaurate and gold. Chlorides act like bromides, but more slowly. Hydrobromic acid gives bromauric acid and gold, and hydrochloric acid acts in a similar manner.

Auroso-auric Bromide (*Aurous Bromaurate*).

The existence of this salt and of the corresponding chloride has been affirmed by Thomsen[2] and denied by Krüss and Schmidt.[3] Peterson[4] established beyond a doubt the existence of the chloride, but was not so successful with the bromide. Finely divided gold precipitated by ferrous sulphate was dried at 105° and kept *in vacuo* over phosphoric anhydride for two weeks. An amount weighing 6.1286 grams was treated with excess of bromine in a closed crucible, the bromine evaporated in a current of dry air, and the crucible then kept *in vacuo* over phosphoric anhydride to constant weight. The mass was finely powdered and again brought to constant weight. This was repeated a number of times. There was of course a slight loss in the powdering and transferring. This has been taken into account, and to avoid complication all the figures have been referred to the quantity of gold originally taken. In the first operation the gold took up 4.7440 grams bromine, in the next 0.2749, then 0.1373, 0.0987, 0.0541, 0.1059, 0.1060, altogether, 5.5209 grams. Thus the first time the gold took up 77.24 per cent of its weight of bromine, and in all 90.08 per cent. To form the compound Au_2Br_4 it must take up 81.07 per cent bromine, and to form auric bromide, $AuBr_3$, 121.6 per cent. This would seem to indicate the existence of the compound Au_2Br_4, especially as a number of experiments showed that finely powdered gold always takes up about 80 per cent of its weight of bromine at the first treatment, and then adds bromine very slowly. If the operation is repeated often enough gold will probably take up 120 per cent of bromine, or even more, as a little is added each time. This action, however, seems due to the presence of moisture. Water readily acts on the compound Au_2Br_4, setting free gold, and this adds bromine. The longer the powder is exposed to the air the more bromine is taken up.

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[1] See Thomsen : *Loc. cit.*

[2] *Loc. cit.* and J. prakt. Chem., (2), **37**, 105.

[3] Ber. d. chem. Ges., **20**, 2640 ; J. prakt. Chem., (2), **38**, 82.

[4] J. prakt. Chem., (2), **46**, 328 : **48**, 88.

It may be urged that auric bromide is first formed and protects the gold from further attack by forming a coating. This seems disproved by the action of ether, in which the tribromide is easily soluble. The auroso-auric bromide seems only slowly affected by anhydrous ether at zero, and this suggested a method of purification. A product prepared by treating gold with bromine seven times and containing 47.3 per cent bromine was treated with ice-cold ether until the liquid, which at first was highly colored, was perfectly colorless. The residue was then dried and analyzed. It contained 61.41 per cent gold and 38.14 per cent bromine (calculated for Au_2Br_4 55.22 per cent gold and 44.78 per cent bromine; for $AuBr$ 71.12 per cent gold; and for $AuBr_3$ 45.08 per cent). It would thus seem to be a mixture of gold or aurous bromide and auric bromide, or of gold or aurous bromide and auroso-auric bromide. The action of water shows that it is not a mixture of auric bromide and gold or aurous bromide in which grains of the auric salt are protected from the solvent action of the ether by a coating of aurous bromide or gold. Aurous bromide and gold are insoluble in water, and would therefore protect from that liquid as well as from ether. True, aurous bromide is decomposed by water but slowly. The substance washed with ether is a mixture of aurous bromaurate, Au_2Br_4, with aurous bromide or gold, probably the latter, for the ethereal solution of auric bromide if not free from traces of moisture reacts with aurous bromide to form bromauric acid and gold. Analysis of the ether solution always showed besides organic oxidation-products more than 3 atoms of bromine to 1 of gold.

The action of bromine upon gold is, therefore, attended with the formation of a steel-blue aurous bromaurate, stable in the absence of water, easily decomposed at ordinary temperatures by water and many organic solvents.

Auric Chloride and Auric Bromide.

These salts are too well known to require much discussion. They easily go into the corresponding halauric acids and gold oxide or gold, the bromide so readily that it is difficult to obtain it pure. If aurous bromaurate is treated with ether and the solution evaporated in a current of air, as recommended by Thomsen,[1] much bromauric acid is obtained unless the ether be pure and dry, and the temperature low. If aurous bromaurate is treated with little ice-cold water and the solution kept cold in a vacuum desiccator over phosphoric anhydride until the water has evaporated, pure gold tribromide is left. Analysis showed 45.35 per cent gold and 54.85 per cent bromine (calculated, 45.08 per cent and 54.92 per cent.) If the temperature is not kept low, there is formation of bromauric acid. Some of the substance which formed from a solution kept at the ordinary temperature contained 3.16 per cent free gold and 2.8 per cent water, corresponding to about 30 per cent of the compound $HAuBr_4.3H_2O$.

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[1] *Loc. cit.*

Chlorauric Acid.

There has been some discussion regarding the existence of the compound $HAuCl_4.4H_2O$.[1] There is no doubt that a compound of the composition $HAuCl_4.3H_2O$ is obtained when the salt is kept in a moderately dry atmosphere, *i.e.*, over sulphuric acid, calcium chloride, or potassium hydroxide. Analysis showed 35.73 per cent to 36 per cent chlorine, and 49.90 per cent to 50.24 per cent gold (calculated 35.98 per cent and 50.04 per cent). Kept for two weeks *in vacuo* over phosphoric anhydride the salt contained 51.86 per cent gold (calculated for $HAuCl_4.2H_2O$, 52.39 per cent). However, the substance was not homogeneous and a considerable portion was insoluble, showing that the loss of water of crystallization was accompanied by decomposition, and making the existence of a compound of the formula $HAuCl_4.2H_2O$ appear improbable. Thomsen bases his belief in the existence of the salt $HAuCl_4.4H_2O$ mainly on thermochemical data. When the compound $HAuCl_4.3H_2O$ is left in the air it rapidly deliquesces. Attempts to identify a definite compound failed. The pasty mass first obtained was spread on clay plates, and the dry substance analyzed. One analysis gave 47.71 per cent gold (calculated for $HAuCl_4.4H_2O$, 47.86 per cent), but another gave 46.32 per cent, and others even lower. Hence if the compound $HAuCl_4.4H_2O$ exists, it readily takes up more water in a moist, and loses water in a dry, atmosphere. The compound $HAuCl_4.3H_2O$, on the other hand, is stable and loses water only with decomposition.

Bromauric Acid.

This substance was obtained by Thomsen's method,[2] which I afterwards modified slightly. The finely powdered and dry gold was left in a covered crucible with an excess of bromine over night, the cover removed, and the bromine evaporated at the room temperature. The mass was then powdered and kept over night in a closed vessel with the requisite quantity of hydrobromic acid and a slight excess of bromine. On exposing to the air, bromauric acid separated. It was powdered and spread on glazed tiles to dry. The air-dried bromauric acid contained 6 molecules of water, though Thomsen gives it the formula $HAuBr_4.5H_2O$. Kept over drying agents it lost 3 molecules water, but again took them up on exposure to the air. Analyses of six samples, treated in different ways, gave 31.16 to 31.47 per cent gold, and 50.81 to 50.91 per cent bromine (calculated for $HAuBr_4.6H_2O$, 31.47 per cent and 51.12 per cent; for $HAuBr_4.5H_2O$, 32.40 per cent and 52.63 per cent). In one lot the hydrogen was determined by combustion.

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[1] Schottländer: Ann. Chem. (Liebig), **217**, 312: Thomsen: Ber. d. chem. Ges., **16**, 1585.

[2] *Loc. cit.*

0.5142 gram salt gave 0.0958 gram H_2O.

	Calculated for $HAuBr_4.6H_2O$.	Calculated for $HAuBr_4.5H_2O$.	Found.
H	2.076	1.757	2.07

Kept over potassium hydroxide, calcium chloride, sulphuric acid, or phosphorus pentoxide, the salt loses 3 molecules of water, but can lose no more without decomposition. Left in a desiccator with potassium hydroxide over night, one sample gave 32.49 per cent gold, another 32.56 per cent gold, corresponding to $HAuBr_4.5H_2O$ (calculated, 32.4 per cent gold), but they lost water on standing longer in the desiccator and took up water on exposure to air. On standing a few days with a drying agent the weight becomes constant, and there is no further loss after a week *in vacuo* over phosphoric anhydride.

Analyses showed from 34.40 to 34.68 per cent gold and 54.35 to 54.75 per cent bromine (calculated for $HAuBr_4.3H_2O$, 34.70 and 54.87 per cent). The energy with which the last molecules of water are held is illustrated by the behavior of the ether solution. The compound $HAuBr_4.6H_2O$ dissolves in chloroform or ether and may be obtained unchanged on evaporation of the solvent. If the ether solution is dried with calcium bromide there is a considerable precipitation of a gold salt, perhaps a double bromide of gold and calcium, and the solution becomes of a much lighter color. If the ether is now evaporated in a current of dry air the compound $HAuBr_4.3H_2O$ is left. Analysis showed 34.16 per cent gold and 54.37

per cent bromine. As the balance might be ether, a combustion was made.

0.6268 gram substance gave 0.0099 gram CO_2 and 0.0734 gram H_2O.

	Calculated for $HAuBr_4.3H_2O$.	Found.
C	....	0.43
H	1.22	1.30

The carbon indicates the presence of a little organic purity.

Silver Salts of Halauric Acids.

Though Schottländer[1] found that silver carbonate gives with chlorauric acid a mixture of silver chloride and auric oxide,

$$2HAuCl_4 + 4Ag_2CO_3 = 8AgCl + Au_2O_3 + H_2O + 4CO_2,$$

Jörgensen's[2] work with silver chlorplatinate makes the existence of silver halaurates probable. If to a solution of chlorauric acid or a chloraurate a silver salt is added in the proportion of 1 equivalent silver to 4 equivalents chlorine, several reactions seem possible. Silver chloraurate may be formed and precipitated as such or it may be decomposed into silver chloride and gold trichloride. Silver chloride may be formed as a primary product so as to leave three-fourths of the chloraurate unchanged, or so as to convert all of it into gold tribromide. The reactions may be represented as follows:

$$HAuCl_4 + AgX = AgAuCl_4 + HX;$$
$$4HAuCl_4 + 4AgX = 4AgCl + AuX_3 + HX + 3HAuCl_4;$$
$$HAuCl_4 + AgX = AuCl_3 + AgCl + HX.$$

Chlorauric acid was dissolved in ice-cold water and a cold solution of silver nitrate (1 mol. to 1 mol.) added. A yellow precipitate was formed at once, but almost immediately it became darker. It was washed and analyzed. In the solution the proportion of gold to chlorine was 1 atom gold to 3.5 atoms chlorine. This and the analysis of the precipitate showed that at least two, and probably all three, of the reactions indicated occur. No simple reaction apparently took place when sodium chloraute or chlorauric acid was treated with silver carbonate or silver nitrate in absolute alcohol. The interpretation of the results was complicated, as the reactions took some time, owing to the insolubility of the silver carbonate, and alcoholic solutions of auric chloride soon deposit gold and retain chlorauric acid, so that the solution showed 4 atoms chlorine to 1 atom of gold. Analysis of the precipitates left no doubt, however.

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[1] Ann. Chem. (Liebig), **217**, 312.

[2] Ztschr. anorg. Chem., **22**, 446.

As sodium chloraurate decomposes before losing its water of crystallization, anhydrous potassium chloraurate was dissolved in absolute alcohol and shaken with silver carbonate. The precipitate contained but little gold, and the solution analyzed at once gave almost exactly 3 (3.07) atoms chlorine to 1 of gold. On standing, the solution deposited gold, and after two days contained 4 atoms chlorine to 1 of gold, thus acting exactly like an alcoholic solution of auric chloride. The reaction, therefore, is:

$$2KAuCl_4 + Ag_2CO_3 = K_2CO_3 + 2AgCl + 2AuCl_3.$$

This seems to be the main reaction even if water is used instead of alcohol.

The action of silver nitrate on an alcoholic solution of potassium chloraurate seems more complicated, as the solution contains 3.4 atoms of chlorine to 1 of gold. Potassium chloraurate and silver salts were shaken together in anhydrous ether but there was no action. Potassium chloraurate is insoluble in anhydrous but not in ordinary ether. In the presence of a little water or alcohol it is more soluble in ether than the sodium salt, though the latter is not insoluble in absolute ether. The remarkable difference in the behavior of sodium and potassium chloraurates toward silver salts may throw some light on the rôle of the water of crystallization in the former. The latter, in solution, acts towards silver salts like a mixture of potassium and gold chlorides. Bromauric acid, in aqueous and alcoholic solutions, acts toward silver salts in about the same way as chlorauric acid, though the reaction is further complicated by the greater instability of some of the products.

The work will be continued, especially in the direction of organic gold compounds.

The analyses were usually carried out by treating the gold compound in water or water and acetic acid with magnesium ribbon. The excess of magnesium was dissolved in acetic acid and the gold washed with nitric acid and water. In the filtrate the halogen was determined as usual. If only the gold content was required this could, in the absence of other non-volatile ingredients, be determined by heating in a crucible, care being taken first to bring the cover to redness so as to decompose any volatile gold compound. The gold salt may also be decomposed by formic aldehyde in alkaline solution. This method gives good results for gold, but cannot be depended upon for halogen.

Contributions from the Sheffield Laboratory of Yale University.

LXXXV.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.

III. THE SOLUBILITY OF ALUMS AS A FUNCTION OF TWO VARIABLES.

BY JAMES LOCKE.

In my second paper in this series[1] I attempted to show that a definite gradation can be traced in the solubility of the alums of aluminium, vanadium, chromium, and iron, severally, with ammonium, thallium, rubidium, and caesium. When the solubilities at 25° of the sixteen compounds considered, expressed in gram-molecules per liter of water, are plotted as a function of the atomic weights of the trivalent metals, a figure of remarkable regularity is obtained. The solubilities of the alums of aluminium, vanadium, and iron, with any given alkali metal, increase with the atomic weights of the trivalent metals; and this increase becomes the more pronounced as we pass from the caesium alums through those of rubidium and thallium, to the ammonium salts, successively. But the alums of chromium, a metal which stands between vanadium and iron in its atomic weight, are much less soluble than those of either of the latter metals. The sharp break in the curves, caused by this behavior of the chromium salts, indicates that although the method of plotting employed illustrates the general gradation of the solubilities, the latter cannot truly be regarded as a function of the atomic weights. The solubilities, as determined, are as follows :

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[1] This JOURNAL, **26**, 166.

$M^{\text{III}} =$	Al.	V.	Cr.	Fe.
$M^{\text{I}} =$ Cs	0.013	0.0204	0.0151	0.045
Rb	0.059	0.177	0.078	0.293
Tl	0.177	0.573	0.212	0.799
NH_4	0.387	1.210	0.407	1.659

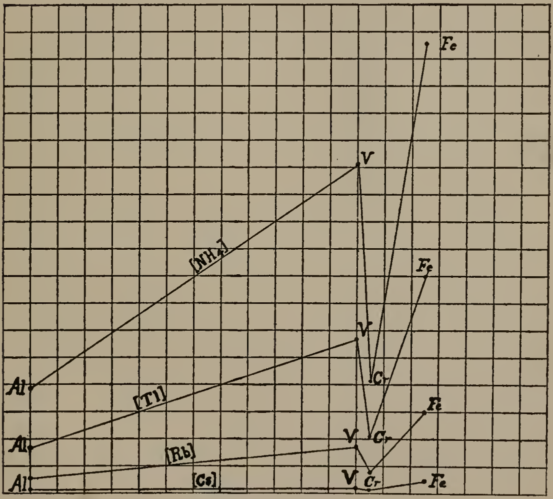

Fig. 1.

Fig. 1 reproduces these relations. For the sake of clearness, the values are slightly increased along the x-axis. The lines joining the vanadium and chromium alums of each univalent metal should, in reality, be nearly perpendicular to the x-axis.

A careful examination of this figure gives, at the outset, one striking result which, if it is also to be observed in solubility charts of other series of homologous compounds, may lead to a great advance in our knowledge of the relative influence of analogous elements upon their compounds. *The lines joining the solubility points of the successive univalent metals with two given trivalent metals, have approximately a common point of intersection.* Thus, the line joining the solubility-points of the caesium alums of vanadium and aluminium, on prolongation, meets that of the thallium alums of the same metals, in the point, $x = 16.25$, $y = 0.11$;[1] the points of intersection of the remaining corresponding lines, vary only slightly from this, and on either side of it. The intersection-points of all the aluminium-vanadium lines with one another follow:

	Cs–Rb.	Rb–Tl.	Cs–Tl.	NH_4–Cs.	NH_4–Rb.	NH_4–Tl.
$x =$	18.1	16.3	16.25	16.0	15.7	15.1
$y =$	1.1	0.11	0.11	1.17	0.15	0.12

The following are the points of intersection of the vanadium-chromium lines:

	Rb–Cs.	Tl–Cs.	Tl–Rb.	NH_4–Cs.	NH_4–Rb.	NH_4–Tl.
$x =$	52.99	52.6	52.65	52.6	52.6	52.53
$y =$	1.2	1.3	0.8	1.4	1.45	5.3

In both of these series the nearest approximation of the points of intersection to a single point is seen to be in the case of those lines which intersect at the greatest angle. The most marked deviation is that of the (AlCs–VCs) and (AlRb–VRb) lines in the first series, and that of the (VTl–CrTl) and (VNH_4–$CrNH_4$) lines in the second; that is, where the lines in question are most nearly parallel, and where, therefore, unavoidable error of experiment would produce the greatest divergence. The various other lines, such as those of (FeM^{I}–CrM^{I}), (FeM^{I}–AlM^{I}), or (CrM^{I}–AlM^{I}), show a similar relation as regards their points of intersection, and it must be assumed, therefore, that *the points representing the solubilities stand in fixed mathematical relation to one another.*

This being so, the derivation of a general formula for the calculation of the solubility of the sixteen alums in question is a comparatively simple matter. The first step involved is the empirical determination of the fixed points, of which the observed points of intersection are approximations. Of these, the three giving respectively the intersections of the lines $(\mathrm{V}M^{\mathrm{I}}\text{–}\mathrm{Al}M^{\mathrm{I}})$, $(\mathrm{V}M^{\mathrm{I}}\text{–}\mathrm{Cr}M^{\mathrm{I}})$, and $(\mathrm{Cr}M^{\mathrm{I}}\text{–}\mathrm{Fe}M^{\mathrm{I}})$ are required.

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[1] The unit on the x-axis being the atomic unit, while that on the y-axis is one-hundredth of a gram-molecule.

The points finally selected, as most nearly satisfying all the points of intersection, are as follows:

$$\text{For } (\mathrm{V}M^{\mathrm{I}}\text{–}\mathrm{Al}M^{\mathrm{I}}) \begin{cases} x = 16.1 \\ y = 0.8 \end{cases}$$

$$\text{For } (\mathrm{V}M^{\mathrm{I}}\text{–}\mathrm{Cr}M^{\mathrm{I}}) \begin{cases} x = 52.61 \\ y = 1.5 \end{cases}$$

$$\text{For } (\mathrm{Cr}M^{\mathrm{I}}\text{–}\mathrm{Fe}M^{\mathrm{I}}) \begin{cases} x = 50.81 \\ y = 0.6 \end{cases}$$

Radii drawn from these points gave, by intersection with perpendiculars raised on the y-axis at points corresponding to the atomic weights of the trivalent metals, the following solubilities in gram-molecules. Under *D* is given the variation from the observed solubilities:

m^{III} =	Al.	*D.*	V.	*D.*	Cr.	*D.*	Fe.	*D.*
m^{I} = Cs	0.012	—0.001	0.0209	+0.0005	0.0169	+0.0018	0.0498	+0.0048
Rb	0.064	+0.005	0.1878	0.0108	0.0734	—0.0046	—0.2776	—0.0164
Tl	0.182	+0.005	0.5670	—0.006	0.2014	—0.0106	0.7922	—0.0068
NH_4	0.382	—0.005	1.209	—0.001	0.4182	—0.0112	1.6643	+0.0016
Average error		+0.001		—0.001		—0.0005		—0.0043

As is seen, the agreement between the observed and calculated solubilities is in the main very satisfactory. In more than half the cases, the difference does not exceed 0.005 gram-molecules. The average molecular weight of an alum is about 300, and the error represented by a difference of 0.001 gram-molecule therefore means about 0.3 gram per liter. As the majority of my determinations were made with quantities of solutions containing about 3 grams of water, an error of this magnitude would therefore represent, on the average, less than a milligram in weight; or in the case of the ammonium alums, where the dissolved salts were determined as sesquioxides, less than 0.5 milligram. A very slight variation in temperature, in the case of the more soluble alums, introduces a still greater error. At 30°, 1 liter of water dissolves 0.467 gram-molecule ammonium aluminium alum, and 0.495 gram-molecule ammonium chromium alum. The increase in solubility for 5° is, therefore, in the one case 0.080, and in the other 0.088 gram-molecule. Assuming that for so short an interval the solubility is directly proportional to the temperature, a variation of ±0°.2 would cause an error of more than 0.003 gram-molecule. The range of solubility of the alums is so great that errors of such magnitudes would have little influence upon the determination of the general solubility relations of the salts; and such relations were all that I had hoped to establish by the work embodied in my last paper. If we take into account the effect which the more or less extensive hydrolytic dissociation of the sulphates of the trivalent metals would have upon the solubility of the alums,[1] the variation between the solubilities, calculated and observed, is in almost every case well within the limit of permissible error. In the derivation of the constants used in this paper, therefore, the calculated results will be taken as correct.

The prolongation of the aluminium-vanadium lines and of the vanadium-chromium lines to their respective points of intersection, yields a series of triangles which have a common base in the line connecting these points. A similar set of triangles is given by the intersection of the vanadium-chromium lines with those of chromium-iron. The resulting figure, somewhat distorted in its proportions, is shown in Fig. II.

The perpendiculars, AAl, BV, CCr, and DFe, and the fixed points, P, Q, and S, being given, the points of intersection of the radii from P, Q, and S with the perpendiculars BV, CCr, and DFe are necessarily determined by the position of the points of intersection of the corresponding radii from P with the perpendicular AAl. Now the points A_1, B_1, C_1, and D_1, represent the solubilities of the caesium alums of the successive trivalent metals; A_2, B_2, C_2, and D_2 those of the rubidium alums, etc. The line A_1P makes a definite angle, θ, with the x-axis, and the points B_1, C_1, D_1, are accordingly determined by the value of this angle. If we substitute rubidium for caesium, θ receives another value, and B, C, and D become B_2, C_2, D_2. The effect of the substitution of any one alkali metal for

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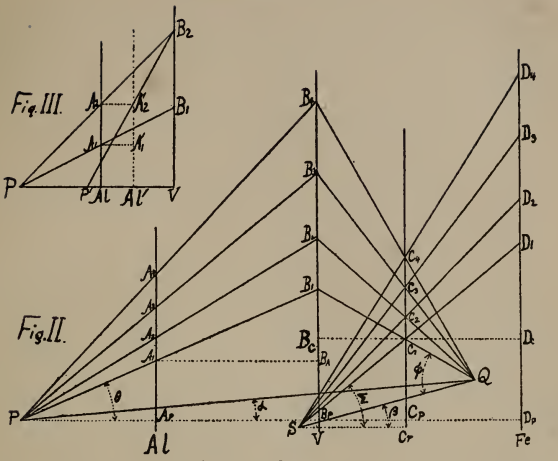
[1] This, of course, also applies to the formation of small quantities of basic salts on evaporation of the solutions for analysis.



Figs. II and III.

another in the alums of a trivalent metal is, therefore, always measurable, directly or indirectly, by the difference in the values of θ peculiar to the alkali metals in question.

The absolute values of the angle θ are fixed by the relative positions of the perpendiculars AAl and BV upon the x-axis; but these do not affect its relative values; for if AAl, for instance, be moved in either direction, the point P still retains its y-value, and therefore the relation

$$\frac{\tan\theta_1}{\tan\theta} = \frac{A_P A_2}{A_P A_1} = \frac{A_P A_2'}{A_P A_1'} = \text{constant.}$$

remains the same in all cases. θ is accordingly a variable peculiar to the alkali metals in the compounds, and independent of the trivalent metals. The same is true of the variable distance $PA (= \rho)$, which depends directly upon the value of θ, in the sense

$$\rho \sin\theta = AA_P = \text{const.},$$

for each of the alkali metals, and without regard to the position of the perpendiculars.

The effect of the trivalent metals upon the solubility is also given by a variable which has a constant value for each. As intercepts of two sides of a triangle by parallel lines, the relations obtain :

$$\frac{A_1B_1}{A_1P} = \frac{A_2B_2}{A_2P} = \frac{A_3B_3}{A_3P} = \dots\dots\dots = k;$$

$$\frac{B_1C_1}{C_1Q} = \frac{B_2C_2}{C_2Q} = \dots\dots\dots\dots\dots\dots = k_1;$$

$$\frac{C_1D_1}{SC_1} = \frac{C_2D_2}{SC_2} = \dots\dots\dots\dots\dots\dots = k_2.$$

These constants, k, k_1, and k_2, are independent of the value of the angle θ, and, therefore, of the univalent metals in the alums. They are also independent of the positions of the perpendiculars AAl, etc. If the relative positions of AAl and BV be altered, for instance, until P becomes P' (Fig. III), the ratio between the new intercepts, $\frac{A_1'B_1'}{A_1'P'}$, is still the same as $\frac{A_1B_1}{A_1P}$, or k.

We have, furthermore, the relation

$$\frac{B_1B_2}{A_1A_2} = \frac{B_2B_3}{A_2A_3} = \dots\; \frac{PB}{PA} = \frac{\rho(k+1)}{\rho} = k+1.$$

Similarly, for the vanadium and chromium alums,

$$\frac{C_1C_2}{B_1B_2} = \frac{C_2C_3}{B_2B_3} = \dots = \frac{C_1Q}{C_1Q + K_1C_1Q} = \frac{1}{k_1+1},$$

and for those of chromium and iron,

$$\frac{D_1D_2}{C_1C_2} = \frac{D_2D_3}{C_2C_3} = \dots = \frac{SC_s + K_2SC_s}{SC_s} = k_2+1.$$

Now A_1A_2 represents the difference in solubility of the aluminium alums of rubidium and caesium ; C_1C_2, that of the chromium alums, etc. If we call the difference in the solubility of the alums of a given trivalent metal with two alkali metals the "increment of solubility for the latter (*e. g.*, Incr. $\mathrm{Al}_{\mathrm{Rb\text{-}Cs}}$), we arrive at the general law :"

The ratio between the increments of solubility of the corresponding alums of two trivalent metals for any two alkali metals is constant.

The constant k indirectly represents, therefore, the effect of the substitution of vanadium for aluminium in the alum of a given univalent metal; k_1 that of chromium for vanadium, etc. And since the value of these constants is not affected by the relative positions of the perpendiculars upon the x-axis, the atomic weights of the trivalent metals have no determining influence upon them. The solubilities cannot, therefore, be regarded as a function of these atomic weights.

The values of the constants k, etc., for the calculated solubilities are as follows:

$$k = 2.2110$$
$$k_1 = 1.9608$$
$$k_2 = 3.0213$$

By substitution we have, furthermore, for the ratio between the solubility-increments of the alums of other pairs of trivalent metals,

$$\frac{C_1C_2}{A_1A_2} = \frac{\text{Incr. Cr}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = \frac{k+1}{k_1+1} = 1.0844;$$

$$\frac{D_1D_2}{A_1A_2} = \frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = \frac{k+1}{k_1+1}(k_2+1) = 4.3604;$$

$$\frac{D_1D_2}{B_1B_2} = \frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. V}_{m^2-m^1}} = \frac{k_2+1}{k_1+1} = 1.3580.$$

Owing to the large errors introduced into the quotient of the observed solubility increments by variations of a few thousandths of a gram-molecule in the solubility determinations, we can expect only an approximate agreement between the above constants and their observed values. The latter, which, together with the variations from the calculated values (D), are given below, are therefore eminently satisfactory. The agreement between them is so marked that there can be no doubt as to the correctness of the law:

$$\frac{\text{Incr. V}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = 3.211. \qquad \frac{\text{Incr. Cr}_{m^2-m^1}}{\text{Incr. V}_{m^2-m^1}} = 0.3377.$$

m^2.	m^1.	Observed.	*D.*	Observed.	*D.*
NH_4	Cs	3.181	−0.030	0.3295	−0.0085
Tl	Cs	3.378	+0.167	0.3561	+0.0184
Rb	Cs	3.404	+0.193	0.4016	+0.0693
NH_4	Rb	3.149	−0.074	0.3185	−0.0192
Tl	Rb	3.356	+0.145	0.3384	+0.0007
NH_4	Tl	3.033	−0.178	0.3197	−0.0316

$$\frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. Cr}_{m^2-m^1}} = 4.021. \qquad \frac{\text{Incr. Cr}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = 1.084.$$

m^2.	m^1.	Observed.	*D.*	Observed.	*D.*
NH_4	Cs	4.118	+0.097	1.021	−0.063
Tl	Cs	3.829	−0.192	1.200	+0.116
Rb	Cs	3.957	+0.044	1.152	+0.068
NH_4	Rb	4.119	+0.098	1.003	−0.081
Tl	Rb	3.770	−0.250	1.127	+0.043
NH_4	Tl	4.410	+0.389	0.927	−0.159

$$\frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = 4.360. \qquad \frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. V}_{m^2-m^1}} = 1.358.$$

m^2.	m^1.	Observed.	*D.*	Observed.	*D.*
NH_4	Cs	4.316	−0.044	1.357	−0.001
Tl	Cs	4.537	+0.177	1.363	+0.005
Rb	Cs	5.411	+1.051	1.606	+0.186
NH_4	Rb	4.164	−0.196	1.322	−0.031
Tl	Rb	4.280	−0.080	1.276	−0.067
NH_4	Tl	4.095	−0.265	1.350	−0.008

The only marked deviations from the calculated constants are in the case of $\frac{\text{Incr. Cr}_{\text{Rb}-\text{Cs}}}{\text{Incr. V}_{\text{Rb}-\text{Cs}}}$, where both increments are so small that even the slightest error of experiment has a great influence upon their ratio; and in some of the ratios obtained with rubidium ferric alum. The observed solubility of this salt is probably somewhat high, owing to the readiness with which it undergoes hydrolysis. The error thus introduced, however, becomes very great only in the ratios $\frac{\text{Incr. Fe}_{\text{Rb}-\text{Cs}}}{\text{Incr. }M^{\text{III}}_{\text{Rb}-\text{Cs}}}$. In the ratios $\frac{\text{Incr. Fe}_{\text{NH}_4-\text{Rb}}}{\text{Incr. }M^{\text{III}}_{\text{NH}_4-\text{Rb}}}$ its influence is hardly felt.

The remaining variables of the triangles *PBQ* and *SCQ*, so far as their values are necessary for the derivation of a general formula for the solubilities, are also to be expressed in terms of θ_1 and k, k_1, etc.

If we call the angle of inclination of the base line *PQ* to the x-axis α, then for the variable angle *BQP*, or φ, we have the expression:

$$\tan\varphi = \frac{PB\sin(\theta-\alpha)}{PQ-PB\cos(\theta-\alpha)} = \frac{\rho\,(k+1)\sin(\theta-\alpha)}{PQ-\rho(k+1)\cos(\theta-\alpha)}.$$

In this formula, α and *PQ* are constant. Substituting for the latter and k their calculated values, we have

$$\tan\varphi = \frac{\rho\sin(\theta-\alpha)}{11.37-\rho\cos(\theta-\alpha)} = \text{R}.$$

Since $$B_1Q = \frac{B_1P\sin(\theta-\alpha)}{\sin\varphi},$$

the variable distance *BQ* becomes:

$$BQ = \frac{\dfrac{\rho(k+1)\sin(\theta-\alpha)}{\tan\varphi}}{\sqrt{1+\tan^2\varphi}}$$

$$= \frac{\rho(k+1)\sin(\theta-\alpha)\sqrt{1+\text{R}^2}}{\text{R}} = M.$$

As the intercepts $BC = k_1CQ$, and, therefore,

$$M = BC + \frac{BC}{k_1},$$

the relation which these intercepts bear to M are

$$BC = \frac{k_1M}{k_1+1} \text{ and } CQ = \frac{M}{k_1+1}.$$

The base line *SQ* makes with the x-axis the constant angle β; the variable angle *BQS* is, therefore, $\varphi+\beta-\alpha$. For the angle *DSQ*, or Σ, we have, as in the case of the angle φ,

$$\tan\Sigma = \frac{CQ\sin(\varphi+\beta-\alpha)}{SQ-CQ\cos(\varphi+\beta-\alpha)}.$$

The value of α is 1°, 5′, 54″, and that of $\beta = 26°, 33', 54''$. Expanding and substituting for these and SQ their corresponding values, and for CQ its equivalent, $\frac{M}{k_1 + 1} = \frac{M}{2.9608}$, we have

$$\tan \Sigma = \frac{M(R + 0.4763)}{6.401\sqrt{1 + \mathrm{R}_2} - M(1 - 0.04763R)}.$$

The distance $AA_P = \rho \sin \theta$. The solubility of the aluminium alums is therefore expressed by the equation

$$S_{\mathrm{Al}} = m + \rho \sin \theta, \qquad (1)$$

m being the y-value of the point P.

For the solubility of the vanadium alums we have

$$BB_P = BB_A + AA_P,$$

and since $BB_A = k\rho \sin \theta$, by addition with (1),

$$S_V = m + \rho \sin \theta + k\rho \sin \theta.$$

Passing in the same manner to the chromium alums,

$$\begin{aligned} CC_P &= BB_P - BB_C \\ &= BB_P - \frac{k_1 M}{k_1 + 1} \sin (\varphi - \alpha) \end{aligned}$$

and, accordingly,

$$S_{\mathrm{Cr}} = m + \rho \sin \theta + k\rho \sin \theta - \frac{k_1 M}{k_1 + 1} \sin (\varphi - \alpha). \qquad (3)$$

The points D_1, D_2, etc., are expressed by

$$\begin{aligned} S_{\mathrm{Fe}} &= m + DD_P. \\ &= m + DD_C + CC_P, \end{aligned}$$

in which $DD_C = CD \sin (\Sigma + \beta)$.

The variable distance CD is given by the equation

$$\begin{aligned} CD &= k_2 CS \\ &= \frac{k_2 CQ \sin (\varphi + \beta - \alpha)}{\sin \Sigma}. \\ &= \frac{k_2 M \sin (\varphi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma}. \end{aligned}$$

Substituting this value for *CD*, we have

$$S_{\mathrm{Fe}} = m + CC_{\mathrm{P}} + \frac{k_2 M \sin (\varphi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma} (\sin \Sigma + \beta),$$

or,

$$S_{\mathrm{Fe}} = m + \rho \sin \theta + k\rho \sin \theta - \frac{k_1 M}{k_1 + 1} \sin (\varphi - \alpha) + \frac{k_2 M \sin (\varphi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma} \sin (\Sigma + \beta).$$

This also serves as a general formula for the solubility (S) of any of the sixteen alums taken into consideration. For if k_2 be made equal to zero, the last term falls away, having the equation in the forms applying to the chromium alums. With k_2 and k_1 equal to zero, the solubilities of the vanadium alums are obtained, and by eliminating the second term as well, those of the aluminium salts. We thus have a general solubility equation, all the terms of which can be referred to two variables: the one of these, θ, applying to the one class of elements in the compounds, the other, k, to the second class. I believe that aside from the instance of additive properties, which the solubilities certainly are not, this is the first case in which a mathematical relation between the corresponding properties of a class of compounds has been found capable of expression.

Below I give the values of θ and ρ for each of the alkali metals, and the solubilities as calculated by the general formula. With the latter, the column D contains the difference between the calculated and observed solubilities, and D' the variation from the values serving as a basis for the derivation of the constants:

	θ.	ρ.
Cs	2° 6′ 5″	10.945
Rb	27° 11′ 19″	12.254
Tl	57° 56′ 4″	20.5406
NH_4	73° 45′ 5″	38.943

In the following the solubilities are expressed in hundredths of a gram-molecule.

				V.			Cr.			Fe.		
	Al.	*D.*	*D'.*	$k = 2.2110.$	*D.*	*D'.*	$k_1 = 1.9608.$	*D.*	*D'.*	$k_3 = 3.0213.$	*D.*	*D.*
Cs	1.192	—0.0108	—0.008	2.06	+0.02	—0.03	1.671	+0.160	—0.020	4.82	+0.32	—0.16
Rb	6.38	+0.328	—0.020	18.90	+1.20	+0.12	7.34	—0.36	0.00	27.76	—1.63	+0.06
Tl	18.21	+0.510	+0.010	56.70	—0.60	0.00	20.13	—1.07	—0.01	79.69	—0.30	+0.47
NH_4	38.18	+0.520	+0.020	120.82	– 0.08	—0.07	41.82	+1.12	0.00	165.26	—0.64	—1.17

In conclusion I may state that while the data now at hand are too few for accurate analysis, such determinations as I have made at temperatures other than 25° indicate that a general-solubility-formula for all temperatures will not be difficult of derivation. I have made determinations at 30° on the caesium, rubidium, and ammonium alums of aluminium, chromium, and iron, and find that the law of the constant ratio of the solubility-increments holds good at that temperature. The values of the constants k, k_1, and k_2, however, vary with the temperature. At 30° $\frac{\text{Incr. Cr}_{m^2-m^1}}{\text{Incr. Al}_{m^2-m^1}} = 1.2$ and $\frac{\text{Incr. Fe}_{m^2-m^1}}{\text{Incr. Cr}_{m^2-m^1}} = 8.3$ in approximate numbers. From the fact that this law obtains at other temperatures, it necessarily follows that at these, as at 25°, the lines joining the solubility-points have common points of intersection. The same formula, therefore, with other constants, obtains at different temperatures. The mathematical relation between the solubilities at 25° can not, accordingly, be a matter of chance.

My thanks are due to Eugene Lamb Richards, Professor of Mathematics in Yale University, for many helpful suggestions embodied in this paper.

NEW HAVEN, April 30, 1901.

LXXXVI.—RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

Second Paper

BY HENRY L. WHEELER.

The treatment of ammonium or potassium thiocyanate with an alkyl halide, in every case which has been carefully examined, gives a normal thiocyanate, R.SCN, as the first product of the reaction. Whenever a mustard-oil is obtained it results from the molecular rearrangement of the normal thiocyanate first formed.

In the case of acyl halides, on the other hand, the products have the isomeric structure,[1] RCO—NCS, and the various chemists who have investigated this reaction have been unable to obtain any positive evidence of the intermediate formation of normal thiocyanates.

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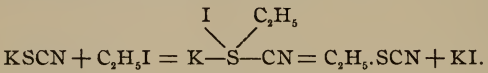
[1] Miquel: Ann. chim. phys., [5], 11, 318 (1877). Dixon: J. Chem. Soc. (London), 67, 565, 1040 (1895); 69, 855, 1593 (1896); 71, 617 (1897); 75, 1388 (1899); 79, 541 (1901). Doran: *Ibid.*, 69, 328 (1896).

The theory generally accepted to account for the action of alkyl halides on potassium thiocyanate is that first proposed by Michael.[1] He assumes that the alkyl group combines with the sulphur and that then potassium halide separates so that a normal thiocyanate results as follows:



$$KSCN + C_2H_5I = K-\overset{I\quad C_2H_5}{\overset{\diagdown\ \diagup}{S}}-CN = C_2H_5.SCN + KI.$$

In another place[2] he mentions the possibility that halides may combine with the nitrogen in this salt. This would then permit of two distinct reactions leading to the formation of isothiocyanates, for he states that all compounds which contain the groups ROCN and RSCN, or ROCNH and RSCNH, will be transformed by heat into the isomeric compounds OC—NR and SCNR, or OCNHR and SCNHR.[3]

He states, as a self-evident fact, that this rearrangement will take place with greater difficulty, the more positive the hydrocarbon radical. As an example is cited the case of allyl thiocyanate,[4] which readily undergoes a molecular rearrangement even at ordinary temperatures, while methyl rhodanide requires heating to a high temperature[5] and the conversion into isothiocyanate, even then is not smooth.

Dixon remarks: "It would seem that the only halogenized compounds which undergo any material conversion into isothiocyanate are those in which the halogen is in direct combination with a negative group."

According to Frerichs and Beckurts[6] a number of chloracetyl derivatives, $ClCH_2CO.R$, $ClCH_2CO_2C_2H_5$, etc., give iso-

[1] J. prakt. Chem., **37**, 509 (1888).

[2] This Journal, **14**, 486 (1892).

[3] In this connection it may be remarked that Victor Meyer was unable to transform ethyl thiocyanate by heat into the isothiocyanate—see Ann. Chem. (Liebig), **171**, 47 (1874)—and Wislicenus and Goldschmidt found that the imidoesters of Pinner decompose on heating alone—see Ber. d. chem. Ges., **33**, 1469 (1900)—although they readily suffer rearrangement when treated with alkyl halides. Cf. Wheeler and Johnson: This Journal, **21**, 186 (1899); **23**, 135 (1900).

[4] Gerlich: Ann. Chem. (Liebig), **178**, 85 (1875).

[5] Hofmann: Ber. d. chem. Ges., **13**, 1350 (1880).

[6] Arch. d. Pharm., **237**, 286, 304 (1899); **238**, 9, 319, 615 (1900).

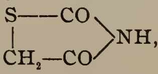
thiocyanates when treated with potassium thiocyanate. In a recent paper[1] from this laboratory it was shown that these supposed isothiocyanates are, without exception, normal thiocyanates.

Since, as far as has been observed, the influence of one $—CO.R$ group ($R = —OAlk.$, $—NXY$, $—CH_3$, $—C_6H_5$, $—C_4H_3S$ thiënyl, etc.) when introduced in place of hydrogen in methyl chloride, does not produce conditions favorable to the formation of isothiocyanates,[2] it seemed of interest to determine whether isothiocyanates would result when two or three of these negative groups are present. Experiments, which may be considered as preliminary to a wider examination of alkyl rhodanides, were undertaken with the following halides :

$$\underset{\text{I.}}{ClCH(CO_2C_2H_5)_2} \qquad \underset{\text{II.}}{ClC(CO_2C_2H_5)_3}$$

Diethylchlormalonate (I) was found to react readily with alcoholic potassium thiocyanate, and the product could be boiled unaltered at reduced pressure. When heated with thiobenzoic acid it gave the diethylmalonate derivative of benzoyldithiocarbamic acid,

$$C_6H_5CO.NHCS.SCH(CO_2C_2H_5)_2,$$

a reaction which establishes the fact that this rhodanide is a normal thiocyanate.[3] This was further confirmed by boiling the rhodanide with concentrated hydrochloric acid, whereupon α-μ-diketotetrahydrothiazole, 
$$\left.\begin{array}{l} S—CO \\ | \\ CH_2—CO \end{array}\right\rangle NH,$$
was obtained.

Tricarbethoxychlormethane (II) proved to be quite unreactive with alcoholic potassium thiocyanate, and little or no thiocyanate was obtained after boiling for a number of hours.[4]

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[1] Wheeler and Merriam : J. Am. Chem. Soc., **23**, 283 (1901).

[2] According to Dixon, $ClCH_2—CO.OH$ gave an amount of "thiocarbimidic" product sufficient to be easily detected, although it was an insignificant fraction of the amount of acid used. J. Chem. Soc. (London), **65**, 390 (1899).

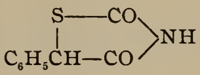
[3] Chanlaroff : Ber. d. chem. Ges., **15**, 1987 (1882) ; Wheeler and Merriam : *Loc. cit.*

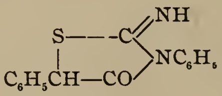
[4] Diethyl ethylchlormalonate, $ClC(CO_2C_2H_5)_2C_2H_5$, also showed a noteworthy inertness. It did not react in alcoholic solutions with potassium thiocyanate, and no reaction was obtained on heating in benzene to 140° to 145° for a number of hours.

The effect produced by the presence of the negative phenyl group was then examined in the case of the following halides:

$ClCH(C_6H_5)CO_2C_2H_5$ III. $BrCH(C_6H_5)_2$ IV. $BrC(C_6H_5)_3$ V.

Ethyl phenylchloracetate (III), when boiled with alcoholic ammonium thiocyanate, gave an oil which distilled unaltered at reduced pressure. When this was heated with thiobenzoic acid it gave the ethyl phenylacetate derivative of benzoyldithiocarbamic acid, $C_6H_5CO.NHCS.SCH(C_6H_5)CO_2C_2H_5$, and therefore this rhodanide is a normal thiocyanate. In accordance with this it gives with hydrochloric acid α-μ-diketo-β-phenyltetrahydrothiazole (VI); and with amines, aniline, etc., it forms compounds which in all probability are pseudothiohydantoïns (VII):


VI.


VII.

When diphenylmethyl bromide (IV) is boiled in benzene solution with potassium thiocyanate, the crystalline product obtained undoubtedly has a mustard-oil structure,

$$(C_6H_5)_2CHNCS.$$

When this compound is heated with thiobenzoic acid, benzoylbenzhydrylamine, $C_6H_5CO.NHCH(C_6H_5)_2$, and carbon disulphide are formed. It reacts with ammonia and organic bases, in the cold, yielding diphenylmethylthioureas,

$$(C_6H_5)_2CH—NHCSNHR.$$

With concentrated sulphuric acid it gives benzhydrylamine, and it is readily desulphurized by boiling with alkaline lead solutions.

If diphenylmethyl bromide is allowed to react with ammonium thiocyanate at ordinary temperatures, in ether or benzene, an oil is obtained which shows no signs of solidifying until it is heated. On distilling at reduced pressure it readily solidifies. On treating the oil with sodium in alcohol, sodium cyanide is formed in quantity, as shown by the Prussian-blue test. On the other hand, the solid product gives no sodium cyanide whatever, under the same conditions. This shows that a normal thiocyanate is the first product of the reaction and this undergoes a molecular rearrangement into the isothiocyanate, as in the case of allyl thiocyanate.

That triphenylmethyl bromide (V) forms a rhodanide has already been shown by Elbs.[1] Although he gives no data in regard to the structure of this rhodanide he shows that it is a very stable compound in regard to heat. He states that it distils at a high temperature without decomposition.

I have found that it reacts with thiobenzoic acid and forms triphenylmethyl thiolbenzoate, $C_6H_5CO.SC(C_6H_5)_3$, and with thioacetic acid it forms the analogous triphenylmethyl thiolacetate $CH_3CO.SC(C_6H_5)_3$. This reaction is characteristic of certain normal thiocyanates. For example, a precisely similar result was obtained with phenyl thiocyanate, C_6H_5SCN, which gave phenylthiolbenzoate,[2] $C_6H_5CO.SC_6H_5$.

In accordance with this, no thiourea derivatives were obtained by the action of ammonia or organic bases. Alcoholic ammonia gave triphenylmethyl amine, triphenylmethylethyl ether, triphenylmethyl carbinol, and ammonium thiocyanate. Moreover, this rhodanide is not desulphurized by boiling with an alkaline lead acetate solution and, on reducing in alcoholic solution with sodium, it responds to the Prussian blue test for cyanides. In other words, the entire behavior of this rhodanide is that of a normal thiocyanate.

It will be seen on comparing the above results that the facts are exactly opposite to what would be expected from the statement of Michael. The least negative or most positive of the above four halides which give rhodanides, forms an isothiocyanate with ease, while the others do not.

That the phenyl group has a less negative influence than the carbethoxy group is shown on substituting these groups in acetic acid and comparing the affinity-constants of the resulting acids :

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[1] Ber. d. chem. Ges., 17, 700 (1884).

[2] Wheeler and Merriam : *Loc. cit.*

CH_3COOH	$C_6H_5CH_2COOH$	$C_2H_5OCOCH_2COOH$
$K = 0.0018$[1]	$K = 0.00556$[1]	$K = 0.0451$[1]

The affinity-constant in the case of acetic acid is increased in the proportion of 1 : 3 by the introduction of the phenyl group, while by the more negative carbethoxy group it is increased in the proportion of 1 : 29.

That the phenyl group has a less negative influence than the carbethoxy group, in other compounds as well, is evident from a consideration of the properties of aniline and urethane.

From the fact that the affinity-constant of acrylic acid ($K = 0.0056$)[2] is somewhat smaller than that of benzoic acid ($K = 0.0060$)[2] it appears that the unsaturated group $CH_2 = CH—$ has a less negative effect than the phenyl group. Nevertheless, allyl rhodanide suffers rearrangement with ease, while benzyl rhodanide, triphenylmethyl rhodanide, rhodanethyl acetate, and even rhodanethylmalonate do not.

The experimental evidence now brought forward goes to show that the tendency to form isothiocyanates is not proportional to the negative character of the radicals, and it will require further work to decide what influence determines the formation, or non-formation, of thiocyanates and isothiocyanates in the reactions in question. At present it is impossible to predict, in new cases, whether or not an alkyl rhodanide will undergo a molecular rearrangement.

EXPERIMENTAL PART.

Diethyl Thiocyanmalonate, $NCSCH(CO_2C_2H_5)_2$.—Diethyl chlormalonate reacts in the cold with an alcoholic solution of potassium thiocyanate. Forty grams of the ester were warmed with an excess of potassium thiocyanate for twenty minutes. On distilling off some of the alcohol and adding water, 40 grams of yellow-colored oil were obtained. Almost two-thirds of this boiled at 169° to 170° at 22 to 23 mm. pressure; a small amount distilled at 150° to 169°. It forms a colorless oil with very little odor, and a nitrogen determination gave:

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[1] Ostwald: Ztschr. phys. Chem., 3, 419 (1889); *Ibid.*, 270; Walker: J. Chem. Soc. (London), 61, 711 (1892).

[2] Ostwald: *Loc. cit.*

	Calculated for $C_8H_{11}O_4NS$.	Found.
N	6.45	6.82

Five grams of this oil were evaporated to dryness with 15 cc. of concentrated hydrochloric acid. On allowing the residue to crystallize spontaneously from water, large, colorless, transparent, four-sided tables melting at 125° to 126° were obtained. A nitrogen determination gave 11.93 per cent. of nitrogen, while the amount calculated for α-μ-diketotetrahydrothiazole is 11.96 per cent.

Diethyl Malonate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCSSCH(CO_2C_2H_5)_2$.—Molecular quantities of the above rhodanide and thiobenzoic acid were warmed in benzene solution for about three hours. The benzene was then removed and the residue, which readily solidified, was purified by dissolving in dilute alkali and precipitating with hydrochloric acid. The small amount of material insoluble in alkali proved to be benzoyl disulphide. On crystallizing the precipitate produced by hydrochloric acid from alcohol, long, bright-yellow, flattened prisms or plates were obtained, melting at 119°. A nitrogen determination gave:

	Calculated for $C_{15}H_{17}O_5NS_2$.	Found.
N	3.94	3.84

The yellow color of this compound, its solubility in alkali, and the above analysis show that this is a benzoyldithiourethane.

Tricarbethoxychlormethane and Potassium Thiocyanate, 35 grams of the former and 15 grams of the latter, were boiled for two days in alcoholic solution. Some potassium chloride separated and the solution became yellow-colored. A portion of the alcohol was evaporated off and water then precipitated an oil, which boiled at 158° to 168° at 21 to 23 mm. pressure. On cooling, yellow needles separated which proved to be pure sulphur. The oil was redistilled at 29 mm. pressure, whereupon about one-half boiled at 163° to 166°. A nitrogen determination in this gave 1.75 per cent nitrogen, while the calculated amount for tricarbethoxymethyl rhodanide is 4.84 per cent. The oil, which was found to contain chlorine, was then distilled at 140 mm. pressure, whereupon almost all boiled at 208° to 210°. This was, therefore, unaltered tricarbethoxychlormethane, which Conrad[1] states boils at 210° at the above pressure. The inertness of this ester and of diethyl ethylchlormalonate, already mentioned, in comparison with diethyl chlormalonate is noteworthy.

Ethyl Phenylchloracetate, $ClCH(C_6H_5)CO_2C_2H_5$.—Phenylchloracetylchloride was prepared from mandelic acid by the process of Bischoff, Walden.[2] This (77 grams) was poured into an excess of alcohol and then distilled at 18 to 17 mm. pressure, whereupon it practically all boiled at 142° to 145°. Out of a yield of 68 grams, 20 grams boiled at 142° and formed a colorless oil with a pleasant, fruity odor, the vapor of which has a slight irritating effect on the eyes. A chlorine determination gave:

	Calculated for $C_{10}H_{11}O_2Cl$.	Found.
Cl	17.88	17.96

Ethyl Phenylthiocyanacetate, $NCSCH(C_6H_5)CO_2C_2H_5$, resulted on warming the chloride for a few minutes with alcoholic ammonium thiocyanate. It forms an oil which distilled for the most part at 182° to 184° at 17 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{11}H_{11}O_2NS$.	Found.
N	6.3	6.9

When 5 grams of this oil were treated with concentrated hydrochloric acid and evaporated to dryness and the residue crystallized from alcohol, beautiful colorless prisms were obtained, melting at 125° to 126°. A nitrogen determination agreed with the calculated amount for α-μ-diketo-β-phenyltetrahydrothiazole:

	Calculated for $C_9H_7O_2NS$.	Found.
N	7.25	7.24

This material is very soluble in alcohol and difficultly soluble in water. It dissolves in dilute alkali.

[1] Ber. d. chem. Ges., 14, 618 (1881).
Ann. Chem. (Liebig), 279, 122 (1894).

Diphenylpseudothiohydantoïn.—When 5 grams of the above thiocyanate were warmed on the water-bath with 2.1 grams of aniline for twelve hours a varnish was obtained which, on taking up in alcohol, deposited needles and plates. The latter, on crystallizing several times from alcohol, melted at 185° to 186°, and a nitrogen determination gave :

	Calculated for $C_{15}H_{12}ON_2S$.	Found.
N	10.4	10.2

The material is insoluble in cold alkali, but readily dissolves on warming. On boiling the solution no aniline could be detected in the distillate.

Ethyl Phenylacetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH(C_6H_5)CO_2C_2H_5$.—Molecular quantities of the rhodanide and thiobenzoic acid were heated in benzene for several hours. On removing the benzene only a trace of carbon disulphide was found. The residue formed a varnish, which, on dissolving in dilute sodium hydroxide and precipitating with hydrochloric acid, gave a solid. This was crystallized from alcohol, in which it is readily soluble, whereupon a mass of thin, yellow plates were obtained, melting at 150° to 154°. A nitrogen determination gave :

	Calculated for $C_{18}H_{17}O_3NS_2$.	Found.
N	3.90	3.91

Diphenylmethyl Isothiocyanate, $(C_6H_5)_2CH—NCS$. — Diphenylmethyl bromide was prepared by the method of Friedel Balsohn.[1] This bromide immediately reacts with an alcoholic solution of ammonium or potassium thiocyanate. The product is an oil, apparently containing some diphenylmethylethyl ether. On distilling at 38 to 37 mm. pressure a portion boils below 222°, then the greater part at 222° to 225°. The latter distillate forms a blue liquid which, on cooling, solidifies. On crystallizing from alcohol it melts at 61° and forms beautiful colorless prisms. It is best prepared by boiling a benzene solution of the bromide with finely powdered ammonium or potassium thiocyanate for several days. When an ether solution of the bromide, free from alcohol, is allowed to stand over potassium thiocyanate for a number of days the product is an oil which consists for the most part of normal diphenylmethyl thiocyanate, since on reduction with sodium it gives sodium cyanide. An analysis of the material crystallized from alcohol and melting at 61° gave:

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[1] Bull. soc. chim. (Paris), 33, 339.

	Calculated for $C_{14}H_{11}NS$.	Found.
N	6.22	6.43

When this material is boiled with alkaline lead acetate it is desulphurized. No sodium cyanide was obtained when this was reduced in alcohol by sodium.

Diphenylmethylacetamide, $CH_3CO—NHCH(C_6H_5)_2$, was formed when 1.5 grams of the isothiocyanate, 3 grams of thioacetic acid, and 10 cc. of benzene were warmed for an hour on the steam-bath. Carbon disulphide was then identified by means of the xanthate test and the residue was crystallized from dilute alcohol, whereupon the material formed a felted mass of colorless needles melting at 146° to 147°. It is very soluble in strong alcohol, from which it crystallizes in the form of compact prisms. A nitrogen determination gave:

	Calculated for $C_{15}H_{15}ON$.	Found.
N	6.22	6.51

This amide is easily saponified by warming with concentrated hydrochloric acid. The long colorless needles thus obtained melt at 270° (benzhydrylamine hydrochloride).

Diphenylmethylbenzamide, $C_6H_5CONH.CH(C_6H_5)_2$, was formed when 4.4 grams of the isothiocyanate, 2.7 grams of thiobenzoic acid, and 10 cc. of benzene were warmed for several hours. On evaporating the benzene, carbon disulphide was found in quantity, and, on crystallizing the residue from alcohol, colorless, silky needles were obtained, melting at 166° to 167°. A nitrogen determination in the sulphur-free material gave:

	Calculated for $C_{20}H_{17}ON$.	Found.
N	4.87	5.21

This amide may be boiled for days with alkali without any apparent saponification. On boiling for a number of days with alcohol and concentrated hydrochloric acid a small amount of benzhydrylamine hydrochloride was obtained, melting, as Leuckart and Bach[1] state, at 270°.

Diphenylmethylthiourea, $(C_6H_5)_2CH—NHCSNH_2$. — One gram of the isothiocyanate was dissolved in alcoholic ammonia, whereupon, on standing over night, beautiful, long, colorless, silky needles separated, melting at 189°. This urea is readily soluble in hot alcohol, and a nitrogen determination gave:

	Calculated for $C_{14}H_{14}N_2S$.	Found.
N	11.5	11.3

Diphenylmethyl-methylthiourea, $(C_6H_5)_2CH—NHCSNHCH_3$. —Two grams of the isothiocyanate were dissolved in alcohol and a 33 per cent solution of methyl amine was added in excess, whereupon an almost immediate separation of colorless, flattened prisms took place. On crystallizing from alcohol they melted at about 152°, and a nitrogen determination gave:

	Calculated for $C_{15}H_{16}N_2S$.	Found.
N	10.9	10.7

This material is easily soluble in alcohol.

Diphenylmethyl-diethylthiourea, $(C_6H_5)_2CH—NHCSN(C_2H_5)_2$, from the isothiocyanate and diethylamine, forms colorless needles, readily soluble in hot alcohol and melting at 112° to 113°. A nitrogen determination gave:

	Calculated for $C_{16}H_{22}N_2S$.	Found.
N	9.39	9.35

Diphenylmethyl-diisobutylthiourea, $(C_6H_5)_2CH—NHCSN(C_4H_9)_2$. — Diisobutylamine combines with the isothiocyanate with evolution of heat, and, on cooling, the material solidifies to a radiating mass of crystals. It forms long, colorless needles from alcohol, which melt at 97° to 98°. A nitrogen determination gave:

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[1] Ber. d. chem. Ges., 19, 2129 (1886).

	Calculated for $C_{22}H_{30}N_2S$.	Found.
N	7.90	8.33

This material is insoluble in alkali, and alkaline lead acetate solutions produce no blackening on boiling.

Diphenylmethylphenylthiourea, $(C_6H_5)_2CH—NH—CSNHC_6H_5$.—The isothiocyanate reacts readily with aniline, when gently warmed, and the mixture solidifies to a white powder. It is very difficultly soluble in alcohol. For analysis it was crystallized from a mixture of toluene and ethyl benzoate; it then melted at 178°. On recrystallizing from glacial acetic acid the melting-point was not altered, and a nitrogen determination gave:

	Calculated for $C_{20}H_{18}N_2S$.	Found.
N	8.80	8.79

It forms a sandy powder which appears to consist of small, compact, colorless prisms. This thiourea has been prepared from diphenylmethylamine and phenylisothiocyanate by Michaelis Linow,[1] who gives its melting-point as 180°.5.

Diphenylmethyl-methylphenylthiourea, $(C_6H_5)_2CH—NH—CS—N(CH_3)C_6H_5$, forms beautiful, long, colorless, slender needles when crystallized from alcohol. It melts at 119° to 120°, and a nitrogen determination gave:

	Calculated for $C_{21}H_{20}N_2S$.	Found.
N	8.43	8.63

Diphenylmethyl-β-naphthylthiourea, $(C_6H_5)_2CH—NHCSNHC_{10}H_7$, forms colorless needles melting at 179°. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}N_2S$.	Found.
N	7.60	7.55

Diphenylmethyl-phenylthiosemicarbazide, $(C_6H_5)_2CH.NHCS(C_6H_5)N—NH_2$.—The isothiocyanate combines smoothly in alcoholic solution with phenylhydrazine. The product is difficultly soluble in alcohol but crystallizes from a mixture of alcohol and ethylbenzoate in colorless plates which melt at 178°. A nitrogen determination gave:

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[1] Ber. d. chem. Ges., 26, 2170 (1893).

	Calculated for $C_{20}H_{18}N_3S$.	Found.
N	12.65	12.62

This product exhibits the curious behavior observed by Marckwald[1] in the case of diphenylthiosemicarbazide, of having two melting-points. If the temperature is maintained at 178°, or a little above, the substance melts completely, but in a few seconds it solidifies and then melts at 198° with effervescence and decomposition. In all probability this behavior is due to a molecular rearrangement in the sense discussed by Busch and Holzmann:[2]

$$\underset{\text{Melting-point 178°.}}{(C_6H_5)_2CHNHCS(C_6H_5)N-NH_2} \longrightarrow$$

$$\underset{\text{Melting-point 198°.}}{(C_6H_5)_2CH-NHCSNH-NHC_6H_5.}$$

Triphenylmethyl Thiolacetate, $CH_3CO.SC(C_6H_5)_3$. — Six grams of triphenylmethylrhodanide[3] and 5 grams of thioacetic acid were heated in 20 cc. of benzene for ten hours. A small amount of carbon disulphide was formed. The residue, on evaporating the benzene, solidified. It was crystallized from alcohol, whereupon beautiful, colorless, twinned prisms were obtained, melting at 138° to 140°. A sulphur determination gave:

	Calculated for $C_{21}H_{18}OS$.	Found.
S	10.06	10.03

Triphenylmethyl Thiolbenzoate, $C_6H_5COSC(C_6H_5)_3$.—Four grams of the rhodanide and 1.9 grams of thiobenzoic acid were heated in 20 cc. of benzene for a number of hours. Carbon disulphide was formed and, on evaporating the benzene, a residue very difficultly soluble in alcohol was obtained. It was readily soluble in benzene and crystallized from a mixture of benzene and chloroform in colorless prisms, melting at 184° to 185°. A sulphur determination gave:

	Calculated for $C_{26}H_{20}OS$.	Found.
S	8.4	8.5

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[1] Ber. d. chem. Ges., **25**, 3098 (1892).

[2] *Ibid.*, **34**, 320 (1901).

[3] *Ibid.*, **17**, 700 (1884).

It was found that this compound could be prepared from potassium thiolbenzoate and triphenylmethyl bromide, a fact that thoroughly establishes its identity.

Triphenylmethyl Thiocyanate and Ammonia.—The rhodanide (10 grams) was dissolved in benzene and this solution was mixed with an excess of alcoholic ammonia and allowed to stand for three days. At the end of this time it was evaporated to dryness and the residue was extracted with hot water. The undissolved residue was then dissolved in benzene, dried, and saturated with dry hydrochloric acid, whereupon triphenylmethylamine hydrochloride separated in the form of small plates, melting at 244°[1] (2.7 grams). The benzene solution was evaporated to dryness and the residue (4.6 grams) proved to be triphenylmethylethyl ether, which crystallizes from alcohol in beautiful stout prisms melting at 83° to 84°.

The aqueous extract, on evaporating almost to dryness, left a flocculent precipitate (1 gram) which, on crystallizing from alcohol, melted at 159°. It was free from sulphur and proved to be triphenylmethylcarbinol. The filtrate from this gave 2 grams of ammonium thiocyanate, calculated 2.4 grams. There was, therefore, no evidence of the formation of a thiourea derivative.

Triphenylmethyl Thiocyanate and aniline gave a mixture of substances from which phenylthiourea was the only material isolated in a state of purity.

Triphenylmethyl Thiocyanate and Phenylhydrazine, when warmed in alcohol, gave colorless prisms melting with effervescence at 201°. A nitrogen determination agreed with the calculated figure for phenylthiosemicarbazide: found, 25.30; calculated, 25.15. Besides this, the unstable triphenylmethanehydrazobenzene described by Gomberg[2] appears to be formed.

In a preliminary experiment, where the substances were mixed at random in order to determine whether they would react, a product was obtained crystallizing in prisms like phenylthiosemicarbazide, but which, after three crystallizations from alcohol, appeared to melt constantly at about 137° (with effervescence). A nitrogen determination in this material gave 10.4 per cent, while the calculated amount for triphenylmethyl-phenylthiosemicarbazide is 10.2 per cent. The writer believes that this product was in all probability a mixture, since subsequent attempts to obtain material in this reaction melting constantly at 137° were without success.

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[1] Elbs: *Loc. cit.*

[2] Ber. d. chem. Ges., 30, 2045 (1897).

The reactions of triphenylmethylrhodanide with thiol acids appear to leave no doubt that the compound is a normal thiocyanate. Theoretically, a compound that easily separates the —NCS group might possibly act as follows:

$$(C_6H_5)_3C\text{—}\boxed{NCS\quad H}SCOCH_3 = (C_6H_5)_3CS.COCH_3 + HNCS.$$

But this reaction has not yet been observed in the case of mustard oils. The invariable reaction is a separation of carbon disulphide and formation of a substituted acid amide. Even benzoyl isothiocyanate, which easily parts with the —NCS group, under certain conditions, with thiobenzoic acid gives dibenzamide.

The action of bases on triphenylmethyl rhodanide is according to what would be expected if the compound had the structure of a normal thiocyanate. But here again, according to Dixon, negative isothiocyanates, CH_3CONCS, are capable of behaving in this manner.

It is noteworthy in this connection that Hemilian and Silberstein[1] were unable to prepare any ureas either from triphenylmethylamine hydrochloride and potassium cyanate or from the base and carbon disulphide.

However, all the experimental evidence thus far obtained points to the curious fact that triphenylmethyl bromide forms a normal thiocyanate, while, not only on account of its negative character but also from analogy with diphenylmethyl bromide, it should form an isothiocyanate.

The following experiments by Dr. T. B. Johnson illustrate some new reactions of strongly negative isothiocyanates. It was found by qualitative experiments that benzoylisothiocyanate reacts with sodium malonic ester, sodium formanilide, sodium phenolate, and sodium acetoacetic ester, and in each case the —NCS group was removed as sodium thiocyanate. In these reactions, as with water, the isothiocyanate appears to act like an acyl halide. Phenyl isocyanate, on the other hand, combines with the sodium salts of certain compounds while the free substances do not react.[1]

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[1] Ber. d. chem. Ges., 17, 742 (1884).

It seemed of interest to determine whether benzoyl rhodanide would behave as a mustard-oil towards phenol ethers, etc., in the presence of aluminium chloride.[2] The action, as perhaps might be expected, was far from satisfactory in regard to smoothness. In one case—with toluene—we obtained a compound which crystallized from alcohol in red prisms and was soluble in alkali. It melted at 135° to 136°, and a nitrogen determination gave 5.64 per cent of nitrogen while the calculated figure for

$$CH_3C_6H_4.CSNHCOC_6H_5 = C_{15}H_{13}ONS$$

is 5.5 per cent.

In the case of phenetol the product proved to be paraethoxythiobenzamide, which formed plates from benzene melting at 158°. Analysis gave 7.95 per cent of nitrogen while the calculated amount for $C_2H_5—OC_6H_4CSNH_2 = C_9H_{11}ONS$ is 7.73 per cent.

It was also established that benzoyl isothiocyanate combines with hydrogen phosphide, apparently to form the phosphourea $C_6H_5CO.NHCSPH_2$. This was obtained as an orange-colored precipitate which dissolved in alkali, forming a red solution. It was very soluble in alcohol but difficultly soluble in benzene. It melted at about 155° to 157°, and a nitrogen determination gave 7.02 per cent of nitrogen, while the calculated amount for C_8H_8ONPS is 7.10 per cent.

NEW HAVEN, CONN., May 22, 1901.

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[1] Paal: Ber. d. chem. Ges., **27**, 974 (1894); Fischer: *Ibid.*, **33**, 1701 (1900).

[2] Gattermann: Ber. d. chem. Ges., **25**, 3525, 3528 (1892).

PHENOXOZONE DERIVATIVES.

BY H. W. HILLYER.

As indicated in a previous paper,[1] when one molecular proportion of picryl chloride, one of pyrocatechin, and two of sodium ethylate, are heated to from 60° to 70° a reaction takes place according to the following equation,

$$C_6H_4(OH)_2 + C_6H_2Cl(NO_2)_3 = C_6H_4O_2C_6H_2(NO_2)_2 + HNO_2 + HCl,$$

and results in the formation of a dinitro derivative of diphenylene dioxide or phenoxozone. The reaction has since been farther studied, and it has been found that in this particular case the yield is not greatly diminished by using alcoholic sodium hydroxide instead of sodium ethylate, and by reducing the relative amount of alcohol used as a solvent. In one case the reaction was carried through in the following manner: 60 grams of picryl chloride and 26 grams pyrocatechin were covered with 1 liter of common alcohol, heated until the picryl chloride was dissolved, and to the mixture a solution of 19.2 grams of sodium hydroxide in a small quantity of water was added. After heating for about four hours, to about 70°, the dinitrophenoxozone precipitated out was filtered off and washed free from the dark impurity present with water and alcohol. When air-dried, the crude substance weighed 50 grams, or 75 per cent of the theoretical.

Acetone is found to be a better solvent than glacial acetic acid or benzene. By dissolving in as little hot acetone as possible about 75 per cent of that dissolved is reprecipitated on cooling.

Reduction with Zinc and Acetic Acid.—On reducing a solution of the substance in glacial acetic acid with zinc dust, a solution is obtained which is colorless, but, on diluting and filtering, the solution becomes wine-red. Ether extracts the colored substance from the dilute acetic acid solution. When the ether solution is shaken with hydrochloric acid it becomes colorless, but on adding sodium acetate the ether again becomes colored. This seems to indicate that a color-base is present whose hydrochloric acid salt is not decomposed by water, while its acetate is hydrolyzed in such a manner that the base can be extracted with ether. The base formed by reduction cannot readily be isolated, but, as appears from work described later, it seems at least probable that one of the oxygen linkages of the phenoxozone is hydrolyzed at the same time that a reduction is effected. The oxidized acetic acid solution is capable of dyeing silk to a dove color. When the solution, immediately after the reduction, is run into a solution of diazotized sulphanilic acid, the mixture turns brown, and on adding sodium hydroxide and common salt, a brick-red precipitate is formed which may be filtered off. It dissolves with difficulty in cold water, but quite easily in hot water, and, on cooling, separates again as a red powder. Its solutions dye silk brown. The reduction with zinc and acetic acid was here abandoned, since it was found that a clean reduction could be effected by the use of tin and hydrochloric acid.

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[1] This JOURNAL, 23, 125.

Diamidophenoxozone.—Ten grams of finely pulverized dinitrophenoxozone are covered with about 150 cc. concentrated hydrochloric acid. Granulated tin is then added. The yellow substance gradually goes into solution, especially on heating on the water-bath. When the nitro compound has nearly all disappeared, the contents of the flask, on cooling, becomes a thick magma of colorless crystals. On adding much water the crystals dissolve. An excess of sodium hydroxide added to the filtered solution precipitates a base along with some tin compounds. The solution is filtered through glass-wool and the precipitate is slightly washed with water. The precipitate is boiled with about 500 cc. of alcohol and filtered. On cooling, the base separates in thin white or light-pink needles, which pack together like felt on filtering. After drying, the first crop of crystals weighs about 5 grams. When the mother-liquor is evaporated to about 200 cc., crystals again begin to separate and, on cooling, a further deposit of crystals may be obtained, especially on adding water to the alcoholic solution.

When equal quantities of alcohol and concentrated hydrochloric acid are used, instead of pure acid, the reduction takes place more quickly, but the base, as purified above, is of a violet-brown color, and crystallizes in thin scales composed of needles laid side by side. They have the same final melting-point as the needles above described, but melt less sharply. The base prepared in this way can be purified by adding stannic chloride and precipitating the tin as sulphide. The sulphide carries down the impurities and the base from the filtered solution is identical with that obtained above. The base melts with blackening at 198° to 200°. A nitrogen determination showed the substance to be diamidophenoxozone.

	Calculated for $C_6H_4O_2.C_6H_2(NH_2)_2$.	Found.
N	13.08	13.17

As a metadiamine it is difficult to diazotize. When nitrite is added to its acidified solution it yields a brown dye-stuff, having the same general color as Bismarck-brown.

A portion of the diamido compound was dissolved in dilute hydrochloric acid. Hydrochloroplatinic acid was added to this solution and produced a whitish precipitate which, when warmed, went into solution, but failed to separate again on cooling, on account of a probable decomposition. Gold chloride gave a greenish precipitate, but on warming there was evident decomposition. To a new portion of the hydrochloride hydrochlorplatinic acid was added, the precipitate filtered off and washed with water, alcohol, and ether. The precipitate is changed by the washing to an orange-brown substance. A part of this latter was air-dried and analyzed by ignition. The analyses are not concordant, but on the whole show that enough hydrochlorplatinic acid is removed by the washing to leave a salt in which the base acts as a monacid base.

	Calculated for	Found.			
	$[C_6H_4O_2C_6H_2(NH_2)_2]_2H_2PtCl_6$.	I.	II.	III.	IV.
Pt	23.2	23.2	24.1	27.1	27.4

By dissolving the base in absolute alcohol and precipitating with an absolute alcoholic solution of hydrochlorplatinic acid and washing with absolute alcohol a salt was obtained, having as high a percentage as is demanded by theory for a compound in which the base acts as a diacid base.

	Calculated for $[C_6H_4O_2C_6H_2(NH_2)_2]H_2PtCl_6$.	Found.	
		I.	II.
Pt	31.2	28.8	31.4
		28.9	30.5
		....	30.4

These results show the weakly basic character of one of the amido groups.

Diacetyldiamidophenoxozone.—About 5 grams of 1.3-diamidophenoxozone and 25 cc. glacial acetic acid were heated to boiling for four or five hours with no apparent change, but on distilling off about 10 cc. of the acid a decided reaction set in and the mass became solid and not easily soluble on adding more acetic acid. The substance was purified by washing with water and recrystallizing from ethyl acetate to which a little alcohol was added to increase the solubility. The product crystallizes from this solvent in very small, pearly-white, glistening scales, which, when filtered, form a mass in the filter which greatly resembles white paper, the different layers added by each filling of the funnel being easily separable when the substance is dry. The crystals melt with blackening at 252°.5 to 253°.

	Calculated for the diacetyl compound.	Found.	
		I.	II.
C	64.4	64.2	64.7
H	4.69	4.69	5.1
N	9.4	8.8	9.0

The amido compound dissolves in dilute sulphuric acid if heat is applied, but on cooling crystals separate. Recrystallization gives radial masses of slender needles of a pale-pink color.

Benzoyldiamidophenoxozone.--From diamidophenoxozone the benzoyl derivative was made by the Schotten-Baumann reaction. The pasty mass first formed, on being treated with alcohol, was disintegrated and left a white powder insoluble even in hot alcohol. The powder was filtered off and a solvent sought for. It is not perceptibly soluble in benzene, toluene, ether, petroleum ether, ethyl acetate, or alcohol at boiling temperatures. It is slightly soluble in boiling amyl alcohol, but can be best purified by dissolving it in hot nitro benzene, from which it separates, on cooling, in a fine powder. After crystallizing twice from nitrobenzene and washing with alcohol the substance melts at 274° to 275°.

Action of Alkali on Dinitrophenoxozone.—When 1,3-dinitrophenoxozone is treated with an alcoholic solution of sodium ethylate, it dissolves with a beautiful carmine color. On adding water, a yellow precipitate is formed insoluble in dilute aqueous alkalies and in alcohol. It has the melting-point and appearance of the original dinitrophenoxozone. The colored solution probably contains an addition-product like that described by Hantzsch.[1]

If instead of sodium ethylate a solution of sodium hydroxide in aqueous alcohol is used, the dinitrophenoxozone easily dissolves, but the resulting compound is different. An alcoholic solution of sodium hydroxide was poured upon 14.7 grams of the dinitro compound. On warming the solution the powder was easily dissolved. Water produces no precipitate. On adding hydrochloric acid to the orange aqueous alcoholic solution a light-yellow substance is precipitated which soon collects in crystals. These can be recrystallized from 50 per cent alcohol, in which the substance is freely soluble in the heat but only slightly soluble in the cold. The product was 14.9 grams.

The substance is very little soluble in cold water and only sparingly soluble in hot water. It melts at 153° to 153°.5. In water solution it slowly reddens blue litmus paper. It slowly dissolves in a cold solution of sodium carbonate, but on warming the solution it dissolves more rapidly with evolution of carbon dioxide. It dissolves slowly in a solution of sodium acetate, coloring it yellow. From its solution in alkali it is not precipitated by acetic acid, though the orange color of the solution is changed to yellow. On adding hydrochloric acid to this yellow solution the substance separates in crystalline flocks. These qualitative reactions point to the presence of a dioxynitrophenol with one hydroxyl group much more strongly acidic than the other. Analysis of the substance yields the following results:

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[1] Ber. d. chem. Ges., **32**, 3137.

	Calculated for $(HO)C_6H_4OC_6H_2(NO_2)_2(OH)$.	Found.	
		I.	II.
C	49.3	49.02	49.1
H	2.74	2.94	2.99

The substance is dioxydinitrophenoxide formed by the hydrolysis of one of the oxygen bonds of the dinitrophenoxozone,

$$C_6H_4O_2C_6H_2(NO_2)_2 + 2NaOH = (NaO)C_6H_4OC_6H_2(NO_2)_2ONa + H_2O.$$

Which of the oxygen bonds is hydrolyzed, or whether, in spite of the sharp melting-point, we have both of the isomeric substances possible cannot now be settled. Argument from analogy is not at all certain in its indications in this case.

The dioxydinitrophenoxide dissolves in ammonia water with considerable ease when the solution is warmed. After boiling until the odor of ammonia is no longer perceptible, the solution, on cooling, deposits long yellow needles in radial masses. They are crystals of the ammonium salt and, on treatment with a solution of sodium hydroxide, they yield ammonia.

The nitrophenol, when treated with an excess of strong solution of sodium hydroxide, yields a garnet-red solution and a crystalline-red precipitate. By filtering this precipitate from the alkaline solution by means of a small Puckal filter and recrystallizing from a small amount of hot water, garnet-red crystal aggregates of a rhombic shape separate. The mother-liquor from the recrystallized substance, on evaporation, deposits stout, light-orange crystals, which are apparently monoclinic and frequently twinned. They soon effloresce on exposure to the air. When dioxydinitrophenoxide is dissolved with two molecular equivalents of sodium hydroxide and the solution evaporated to the point of crystallization, two kinds of crystals like those above separate at the same time: first, garnet-red, rhombic aggregates; secondly, orange-red, sixsided, apparently monoclinic crystals. The latter, on standing in the air, effloresce, and in efflorescing show a strong tendency to cleave parallel to the crystal faces, especially parallel to the clinopinacoid. The two kinds of crystals can be separated by sifting, after efflorescence of the second kind. The latter, dissolved in hot water, crystallizes out on cooling the solution sometimes in the original form, but more often in orange-yellow needles. These needles do not lose weight when heated to 110° to 115°. Analysis to determine the sodium is difficult on account of the vigor of the reaction when the salt is heated with sulphuric acid.

	Calculated for mono-sodium salt.	Found. I.	II.	III.
Na	7.3	6.40	6.85	6.75

In another experiment a slight excess of alkali was used, and, on evaporating, there was a deposit of the dark rhombic aggregates, and mixed with them an equal quantity of stout, well-formed, ruby-colored crystals with well developed crystal faces. The latter do not effloresce. Separated by hand and recrystallized, each of these deposits, first a little of the other kind, and then from the mother-liquor a crop of the kind selected.

The ruby crystals, on drying over sulphuric acid *in vacuo*, lose nearly 1 molecule out of the three molecules of water of crystallization and yield, on evaporation with sulphuric acid, an amount of sodium sulphate confirming the theory, though not very closely agreeing with it.

	Calculated for sodium salt + $3H_2O$.	Found. I.	II.
H_2O	4.6	4.49	4.33
Na_2	11.79	11.99	11.05

The recrystallized garnet salt appears in massive crystals of the color of potassium ferricyanide. These, over sulphuric acid *in vacuo*, lose 4.23 and 4.52 per cent.

On heating in an air-bath from 110° to 115° more weight was lost, amounting with that *in vacuo* to 11.3 per cent (calculated for $3H_2O$, 13.8 per cent), and on heating with sulphuric acid the amount of sodium sulphate indicates that the sodium salt has the composition below :

	Calculated for Na_2 in salt + $3H_2O$.	Found.
Na	13.8	10.93

On account of a lack of material these results could not be made more satisfactory, but they seem to show that the garnet salt is like the ruby salt, with perhaps an admixture of the monosodium salt. The nitrophenol, whether set free from the ruby salt, from the garnet salt, or from the needles of the monosodium salt, always has the same melting-point.

When dinitrodioxyphenoxide is treated with an amount of sodium hydroxide, just insufficient to dissolve it, a yellow solution is obtained, and, on evaporating to a small bulk, orange needles separate in tufts. When removed from the mother-liquor and allowed to dry in the air, and more quickly over sulphuric acid, they turn bright scarlet, probably from loss of water. Silver nitrate in excess was added to a solution of this salt, a yellow amorphous precipitate was formed, and immediately filtered off and washed slightly. On drying, the yellow silver salt changed to a brilliant scarlet and yielded, on analysis :

	Calculated for the mono-silver salt.	Found.	
		I.	II.
Ag	27.06	27.3	27.6

Dioxydinitrophenoxide and zinc oxide mutually dissolve one another when covered with water to yield an orange solution, from which, through an accident, the zinc salt was not isolated.

The dimethyl compound of the nitrophenol was made by the method of Lander.[1] In a 250 cc. flask 4 grams of the phenoxide was treated with 8 grams silver oxide, 15 grams methyl iodide, and about 50 cc. benzene. After the first slight spontaneous action was over, the mixture was heated on the water-bath for about an hour It turned yellow in consequence of the formation of silver iodide. After driving off the excess of benzene, the residue was extracted with boiling alcohol, and from this, on cooling, a solid separates not soluble in a dilute, cold solution of sodium hydroxide, either aqueous or alcoholic. When heated, however, it dissolves to yield a yellow solution, and with cold concentrated alcoholic soda it yields a solution of a fine carmine color. After crystallizing three times from hot alcohol the substance melts at 119° to 120°. This substance will be further studied.

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[1] J. Chem. Soc. (London), 1900, 729.

When the dioxydinitrophenoxide is treated with tin and hydrochloric acid it is reduced, but when an attempt is made to isolate the base by precipitating the tin with hydrogen sulphide and treating the filtrate from this with an alkali, the solution turns violet and no base can be isolated. The hydrochloride can be obtained as a light violet mass by evaporating its solution in an atmosphere of hydrogen sulphide. The instability of the base and its turning violet strongly suggest the compound obtained when dinitrophenoxozone is reduced with zinc and acetic acid and also suggests the possibility that, in the latter case, the reduction may have been accompanied by a hydrolysis of one of the oxygen bonds.

In attempting to generalize the reaction described above, the following facts have been gathered : Under the conditions used above, picryl chloride and alkali, with alizarine, do not produce a condensation-product. No attempt has yet been made to bring about the change at a higher temperature.

Nitroparadibrombenzene, when treated with one molecular proportion of pyrocatechin and two molecular proportions of sodium hydroxide in alcoholic solution, yields no nitrite or workable product.

When dinitrobrombenzene (Br,NO_2,NO_2 : 1,2,4) is treated in the same way with pyrocatechin and alkali, it yields no nitrite but a considerable quantity of the ethyl ether of dinitrophenol (m. p. 84° to 85°). In this case the action takes place more readily with the alcohol present than with the pyrocatechin.

Successful attempts to bring about condensations similar to the first described have so far been made in two other cases. Nitropyrocatechin (OH,OH,NO_2 : 1,2,3), made by the action of an ethereal solution of nitric acid on an ethereal solution of pyrocatechin and subsequent steam distillation, yields with picryl chloride a condensation-product. A nitrite is formed and a product is obtained consisting of yellow crystals. Further study of this compound was interruptedby the departure from the University of the student having it in charge.

Picryl chloride and alkali act readily on pyrogallol with the formation of much nitrite and chloride, but the isolation of the compound shows much difficulty. Using common alcohol and sodium hydroxide as the condensing agents, only a very small quantity of the desired product could be obtained, the greater part of the picryl chloride being changed to sodium chloride and sodium picrate, but, by the use of sodium alcoholate in absolute alcohol, a more satisfactory yield was obtained. In its final form the process was as follows: 10 grams picryl chloride and 5 grams pyrogallol were dissolved in 200 cc. hot absolute alcohol which had been redistilled from sodium. This, after the addition of 0.92 gram of sodium dissolved in from 40 to 50 cc. absolute alcohol, was heated one-half hour on the water-bath; a second portion of 0.92 gram of sodium in 40 cc. alcohol was then added and the whole heated from five to six hours. On adding the first portion of sodium a slight brownish precipitate separated, which proved to be mainly sodium chloride. On adding a second portion a heavy precipitate, chiefly of sodium nitrite, came down. The precipitate was filtered off, the filtrate evaporated to dryness, the residue washed with hot water several times and crystallized from acetone, and then several times from glacial acetic acid. From acetone it comes down in the form of a light-yellow powder; from acetic acid as broad, brown, transparent spikes, collected in tufts. The melting-point of the substance, crystallized three times from acetic acid, is 258° to 258°.5 with decomposition.

It is insoluble in cold water, sparingly soluble in hot water, benzene, and ether, more soluble in absolute alcohol, phenol, and ethyl acetate, and very soluble in nitrobenzene, glacial acetic acid, and acetone. It is soluble in dilute alkalies and reprecipitated from them unchanged by the addition of an acid, but in strong alkali it is decomposed, slowly in the cold and rapidly with heat, giving a dark-brown solution from which a tarry mass is precipitated by a strong acid. The first analyses were made with some of the substance crystallized but twice from acetic acid. The crystals were washed with alcohol and dried in an air-bath at 150° for two hours. The first two combustions were lost in consequence of explosions. This was avoided in the other cases by mixing the substance with powdered copper oxide. The result of combustion I. not being very satisfactory, the substance was crystallized a third time and analyses II. and III. made.

	Calculated for $C_6H_3(OH)—O_2—C_6H_2(NO_2)_2$.	Found. I.	 II.	 III.
C	49.65	49.4	49.42	....
H	2.07	2.49	2.07	....
N	9.65	....	....	9.53

In view of these analytical results and of the fact that chloride and nitrite were formed and from the phenol-like character of the resulting compound in its conduct toward dilute alkali, the reaction seems to have taken place normally and to have resulted in the formation of a hydroxydinitrophenoxozone.

Two isomeric substances may, according to theory, be formed, but it is not now possible to tell which one is formed.

In the preparation of the phenoxozone derivative, a heavy precipitate is formed, as has already been mentioned. This consists largely of sodium chloride and sodium nitrite, but it has another constituent which is phenol-like in its character, being readily soluble in dilute alkalies and reprecipitated from them by acids. It is very much of the nature of the compound obtained by dissolving the phenoxozone derivative in strong alkali and reprecipitating with an acid. From this we might expect that the alkali present had decomposed the condensation product as rapidly as it was formed until the alkali had become so dilute that it was no longer able to effect decomposition. Since ammonium hydroxide does not decompose the hydroxydinitrophenoxozone, except very slowly, even when hot and concentrated, the idea was suggested to try to improve the yield by using an alcoholic solution of ammonia in place of the alcoholate or hydroxide of sodium. On trying the alcoholic solution of ammonia, picramide was obtained in fair quantity, together with tarry by-products, the reaction taking place to a great extent as though the pyrogallol were not present.

As yet no definite results have been obtained in determining the character of the decomposition-product obtained by the action of strong alkali on the phenoxozone derivative, the principal difficulty being the impossibility of purifying the resulting compound. The indications are that a new compound is formed ; that it possesses a strong acid character, since it is not precipitated from alkaline solutions by acetic acid, but is precipitated by hydrochloric or sulphuric acid. From these facts it is probable that the alkali has acted to split open one of the oxygen bonds, giving a trihydroxy compound having one of the hydroxy groups in the same phenyl radical which imparts to it its strong acid properties.

The hydroxyphenoxozone was reduced with tin and hydrochloric acid. When the reduction was complete and the solution cooled a white precipitate was formed which consisted of the hydrochloride of the base. This was filtered off through glass wool, dissolved in a small quantity of water, and the free base precipitated by the addition of sodium carbonate. In order to purify it, it was dissolved in hot alcohol and water added until it became turbid. On standing, fine, needle-like crystals separated out, melting at 252° to 253°. The free base is soluble in alkali, but it is apparently decomposed by it, for it is not precipitated unchanged by neutralizing with hydrochloric acid, but instead a brown, amorphous substance is thrown down. The base is soluble in alcohol and acetone, but difficultly soluble in water and the common organic solvents.

The work on the action of picryl chloride on pyrogallol was carried out by Mr. R. D. Hall, to whose skill and perseverance I am greatly indebted.

LABORATORY OF ORGANIC CHEMISTRY,
UNIV. OF WISCONSIN, May 20, 1901.

THE ACTION OF BENZOYL CHLORIDE ON AMMONIUM SULPHOCYANATE.

BY GIDEON BENSON AND H. W. HILLYER.

Benzonitrile being one of the best non-aqueous solvents for many salts, and these solutions exhibiting most interesting variations from the laws laid down for aqueous solutions, a method is desirable for its preparation, more prolific in its yield than the methods now known. While this desire has not, by the present work, been fulfilled in any complete way it is still thought best to put on record the results obtained.

The leading thought in this research was that dibenzoylthiourea might, on heating, break up into benzonitrile, hydrogen sulphide and carbon dioxide according to the equation:

$$(C_6H_5CONH)_2CS = 2C_6H_5CN + H_2S + CO_2.$$

Since ammonium sulphocyanate and thiourea are mutually changed into one another at 170°, a state of equilibrium being established, it was decided to use the former instead of the latter and study the effect of heating it with benzoyl chloride.

Ten grams of ammonium sulphocyanate were heated with 45 grams benzoyl chloride, in a retort with a reflux condenser, until no more hydrochloric acid was evolved, and the residual products distilled. The greater part of the distillate comes over between 190° to 210°, and crystallizes on cooling, forming a mass saturated with a liquid having the odor of benzonitrile. The crystals were shown to be benzoic acid, and the oil, by its boiling-point and hydrolysis to benzoic acid, was shown to be benzonitrile.

In order to study the products formed besides benzoic acid, benzonitrile, and hydrochloric acid, a new experiment was made. The mixture of benzoyl chloride and ammonium sulphocyanate was heated in a sulphuric-acid bath to 190°. The gases generated were passed through water to take up the hydrochloric acid and through lime-water to take up carbon dioxide. The gas not dissolved was found to be combustible with a blue flame and the odor of sulphur dioxide. Hydrogen sulphide could be detected in some cases or phases of the reaction, but was not always present even when the gas, as collected above, was combustible. The latter was found to be carbon oxysulphide.

An explanation of the above reaction was suggested by the work of Kekulé[1] in studying the action of benzoic acid on ammonium sulphocyanate. These substances, when heated together in the proportion of their molecular weights to 150° to 170°, react together, setting free carbon oxysulphide, ammonia, carbon dioxide, and carbon disulphide, and forming benzamide. The reactions involved are represented by the following equations:

$$C_6H_5COOH + NH_4CNS = C_6H_5COONH_4 + HCNS;$$
$$C_6H_5COONH_4 + HCNS = C_6H_5CONH_2 + COS + NH_3;$$
$$2COS = CO_2 + CS_2.$$

Under the influence of heat, in the presence of potassium benzoate, the amide was supposed to be dehydrated to benzonitrile.

Two series of equations, yielding the same final products, may be suggested to explain the product formed in the case now being studied:

$$C_6H_5COCl + NH_4CNS = C_6H_5COCNS + NH_4Cl;$$
$$C_6H_5COCl + NH_4Cl = C_6H_5CN + H_2O + 2HCl;$$
$$C_6H_5COCNS = C_6H_5CN + COS;$$
$$C_6H_5COCl + H_2O = C_6H_5COOH + HCl;$$

and

$$C_6H_5COCl + NH_4CNS = C_6H_5CONH_2 + HCl + HCNS;$$
$$C_6H_5COCl + HCNS = C_6H_5COCNS + HCl;$$
$$C_6H_5COCNS = C_6H_5CN + COS;$$
$$C_6H_5CONH_2 + C_6H_5COCl = C_6H_5CN + C_6H_5COOH + HCl.$$

Either of these series, when summarized, may be expressed thus:

$$3C_6H_5COCl + NH_4CNS = 2C_6H_5CN + C_6H_5COOH + 3HCl + COS.$$

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[1] Ber. d. chem. Ges., 6, 113.

The second series appears, on the whole, the more probable.

To test the reaction further and to determine experimentally whether or not the amount of the products obtained by the reaction supported the hypothetical summarized equation, the reaction was carried through again and made as nearly quantitative as possible. The substances were taken in the proportions of 1 molecule of ammonium sulphocyanate to 3 molecules of benzoyl chloride.

Ammonium sulphocyanate (7.6 grams) and benzoyl chloride (42.1 grams) were brought together in a retort so placed that the neck of the retort was inclined upward. The mixture was heated to 185° to 200° until action appeared to be over or until gases were no longer evolved. The gases evolved were passed first through water to take up the hydrochloric acid, then through potassium hydroxide to take up carbon dioxide and hydrogen sulphide. Some gas not absorbed by these was collected over water. When ignited, it burned with a blue flame and yielded sulphur dioxide, but before ignition it had no odor and gave no test for hydrogen sulphide with lead acetate paper. These qualitative tests sufficiently indicate the presence of carbon oxysulphide.

When the solution of potassium hydroxide through which the gases had passed was tested with barium hydroxide, it gave evidence of the presence of a carbonate, and, when tested with lead acetate, it gave evidence of the presence of a sulphide.

The hydrochloric acid absorbed in the wash-bottle was determined as chloride and found to amount to 10.08 grams. According to the theory the quantity used should have yielded 10.95 grams.

The reaction-product in the retort was then distilled over a free flame. All distilled over except 2.6 grams of a tarry residue and a small amount of yellow crystals in the neck of the retort.

The distillate was reddish-brown and crystallized on cooling. The first distillate was redistilled. About half passed over below 200°. The residue was nearly colorless. Both portions were treated with sodium carbonate and shaken out with ether. The ethereal solutions were dried and the ether evaporated. There was a residue containing 15 grams of pure benzonitrile passing over between 190° to 192° and leaving a black, oily mass, containing benzonitrile and benzoic acid. These were separated by sodium carbonate and extracted with ether, and in this way 1 gram more of benzonitrile was obtained.

The sodium carbonate solutions were acidified with hydrochloric acid, and the benzoic acid which was precipitated was filtered off, and after being dried weighed 11.25 grams. Since benzoic acid is soluble in water to the extent of 3 parts per thousand and the total wash-water was 920 cc. we should add to the amount weighed 2.75 grams, making in all 14 grams. Theoretically, the amount of benzonitrile obtained would be 20.6 grams and of benzoic acid 12.2 grams.

The weight of nitrile obtained by the experiment, however, was 16 grams, or 78 per cent of the theoretical, while the weight of acid was 14 grams, or 115 per cent of the theoretical. These variations can easily be accounted for by the presence of a very small amount of moisture in the ammonium sulphocyanate. The residues must also be considered. From 42.1 grams benzoyl chloride are obtained :

	Theoretical. Grams.	Found. Grams.
Benzoic acid	12.2	14.00
Hydrochloric acid	10.97	10.08
Benzonitrile	20.97	16.00

By this method a yield of 38 per cent of the benzoyl chloride used was obtained as benzonitrile.

The three methods mentioned in the literature which give the product are those of Fehling,[1] Letts,[2] and Henry.[3]

Fehling made benzonitrile by heating ammonium benzoate. The yield was 50 per cent of the benzoic acid used, but the process is a very slow one, requiring five days to give 6 ounces of product.

Letts, by heating 2 molecules of benzoic acid with 1 molecule of potassium sulphocyanate obtained hydrogen sulphide, carbon dioxide, and benzonitrile, the yield of the last being 34 per cent of the benzoic acid used, or 80 per cent of the amount predicted by the equations:

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[1] Ann. Chem. (Liebig), 49, 92.

[2] Ber. d. chem. Ges., 5, 675.

[3] *Ibid.*, 2, 307.

$$C_6H_5COOH + KCNS = C_6H_5COOK + HCNS;$$
$$C_6H_5COOH + HCNS = C_6H_5CONH_2 + COS;$$
$$C_6H_5CONH_2 = C_6H_5CN + H_2O.$$

Henry found that, when benzamide and phosphorus pentasulphide were distilled together, hydrogen sulphide and benzonitrile are obtained. By this method about 42 per cent of the benzamide used was obtained in the form of pure nitrile.

Taking into account the price and availability of the initial substances in the four methods there seems to be no great advantage in favor of either one.

LABORATORY OF ORGANIC CHEMISTRY,
UNIV. OF WISCONSIN, May 24, 1901.

THE REDUCTION OF COPPER BY SOLUTIONS OF FERROUS SALTS.

BY H. C. BIDDLE.

The genesis of the great deposits of native copper is a subject which has invited considerable attention. The commonly accepted theory that the copper has been deposited from its compounds by solutions of ferrous salts is based on the close relation between the reduced metal and the ferric oxide contained in the associated minerals.[1] It is consequently of interest to determine experimentally under what conditions such reduction may occur. Some investigation has already been conducted in this direction.

As early as 1861 Knop succeeded in forming cuprous hydroxide by treating a mixture of cupric and ferrous sulphates with alkaline carbonate.[2] In one instance he speaks of obtaining traces of copper. In 1864 Wibel repeated Knop's experiments,[3] but was unable to verify the latter's statement regarding the reduction to metallic copper. When, however, a mixture of ferrous and cupric hydroxides, formed by adding potassium hydroxide to a solution of the sulphates, was heated to 210° C., traces of copper were obtained. Solutions of the sulphates and coarsely powdered wollastonite, subjected to the same treatment, yielded a like result. The separation of metal, however, was slight and the part played by the ferrous hydroxide in the reduction was, at the time, somewhat questioned.

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[1] Raphael Pumpelly: Am. J. Sci., 2, 353 (1871); R. D. Irving: Mon. U. S. Geol. Surv., No. 5, p. 420 (1883).

[2] A. Knop: N. Jahrb. für Min., (1861), p. 513.

[3] Ferd. Wibel: "Das Gediegen-Kupfer und das Rothkupfererz," (1864), p. 20.

In 1867 Braun observed the partial deposition of copper from a mixture of ferrous and cupric salts when these were dissolved in large excess of ammonium carbonate.[1] The same year Weith secured a ready reduction in the presence of tartaric acid.[2]

He failed to note, however, that under the same conditions the organic acid itself will slowly reduce the copper salts. A mixture of calcium hydroxide with a solution of ferrous and cupric sulphates, was allowed to stand for several weeks. The precipitate thus obtained, when treated with acetic acid, left a residue of cuprous oxide and copper. Strangely enough, Weith overlooked the fact that cuprous oxide with acetic acid yields cupric acetate and metallic copper. In 1869 Hunt[3] stated that copper could be obtained by the action of cupric chloride on freshly precipitated ferrous hydroxide, or carbonate. Nothing is given, however, to indicate that the metal was actually detected by isolating it from ferric hydroxide precipitated along with it.

The deposition of copper by solutions of ferrous salts is a reversible reaction governed by the ordinary laws of chemical equilibrium.

It is to Arrhenius largely that we owe the view that certain substances in solution are more or less dissociated into electrically charged parts, or ions. This theory has proved of the highest value in affording an insight into the principles of chemical reactions. Different substances differ much in their tendency to pass into the ionic form, and this tendency is greatly influenced by external conditions, particularly by the nature of the solvent. The chief source of ions is the dissociation of electrically neutral molecules such as occurs in the aqueous solutions of salts, acids, and bases. They may further be formed from electrically neutral substances which enter the ionic condition by partially, or wholly, appropriating the electric charge of ions already present.[1]

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[1] E. Braun : Ztschr. Chem., (1867), p. 569.

[2] W. Weith : *Ibid.*, (1867), p. 623.

[3] Sterry Hunt : Compt. rend., (1869), p. 1357.

As an example of this mode of formation may be mentioned the reduction of ferric salts by the action of metallic iron:

$$2FeCl_3 + Fe = 3FeCl_2.$$

The solution of metallic copper in ferric chloride is an action of the same nature:

$$Cu + 2FeCl_3 = CuCl_2 + 2FeCl_2.$$

As is seen, the deposition of copper by a ferrous salt would be the reverse of this last reaction.

The conditions under which such reduction should occur may be readily determined. In a system which contains a solution of iron and cupric salts in contact with metallic copper, and in which the several constituents have attained a constant value, a condition of equilibrium subsists, on the one hand, between ferric, cuprous, ferrous, and cupric ions

$$(Fe''' + Cu' \rightleftarrows Fe'' + Cu''),$$

and, on the other hand, between ferric, ferrous, and cuprous ions, and the active mass of the metallic copper

$$(Cu + Fe''' \rightleftarrows Fe'' + Cu').$$

If a, b, c, d, respectively, represent the active masses of the ions in the first instance, an equation of equilibrium may be thus formulated: $\frac{a \cdot b}{c \cdot d} = K$.[2] The active mass of the copper is of constant value, hence in the second instance, retaining the same letters, we have the expression $\frac{a}{b \cdot c} = K'$.

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[1] F. W. Küster: Ztschr. Elektrochem., 4, 105.

[2] W. Nernst: "Theoret. Chem.," p. 358.

The precipitation of copper would then be favored by increasing the concentration of ferrous, cuprous, and cupric ions and by decreasing that of the ferric ions.

The deposition of the metal, consequently, should depend on the relative active masses of the ions present.

This assumption is fully sustained by the experimental evidence which follows:

The precipitation of metallic copper by solutions of ferrous salts is a reversible action, whose direction in any case is determined by the relative concentration of the ferrous, ferric, and copper (cuprous and cupric) ions.

(*a*) In a solution containing an appreciable quantity of ferric ions, or in which these would be formed in the course of the reaction, metallic copper will not be deposited.

This is shown in the inability of ferrous chloride, or sulphate, to reduce corresponding copper salts, even though the mixed solutions stand for an indefinite period. This inaction is, indeed, to be expected when we consider that solutions of ferric salts, as the sulphate and chloride, easily dissolve metallic copper with the formation of a cupric salt.

From this it is readily understood why Wibel[1] obtained no reduction of the copper salts on heating the mixed sulphates together to 210° C. in solution.

(*b*) In a solution containing few ferric ions, and in which the reaction does not result in their appreciable increase, a sufficient concentration of ferrous and copper ions will result in the deposition of metallic copper.

The tendency of ferrous to reduce copper salts is shown in the precipitation of cuprous sulphocyanate by the action of the ammonium salt on a solution of ferrous and cupric chlorides. The same tendency appears in the formation of cuprous chloride on treating cupric oxide with a solution of ferrous chloride.[2] From an emulsion of ferrous and cupric hydroxides, after long standing, crystals of cuprous oxide can be separated. That further reduction is largely determined by the concentration of the cupric and ferrous ions, appears probable from the action of ammonium carbonate on a solution of ferrous and cupric chloride.[1]

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[1] "Das Gediegen-Kupfer und das Rothkupfererz," p. 20.

[2] Sterry Hunt: *Loc. cit.*

The precipitate first formed on adding the carbonate to the mixed chlorides dissolves in an excess of the precipitant to a yellow liquid, from which, on standing twenty-four hours, a slight but brilliant mirror of metallic copper is deposited on the walls of the vessel.

The influence of the concentration of the ions on the reduction of copper is clearly shown in the behavior of the mixed carbonates under varying conditions.

When a solution of cupric and ferrous chlorides (1 mol. $CuCl_2$: 2 mol. $FeCl_2$) is added to a considerable excess of sodium carbonate, a greenish precipitate of the carbonates is obtained, which undergoes but slight change on standing. Such a solution, indeed, would naturally little favor the separation of metallic copper, since the highly ionized alkaline carbonate would greatly decrease the active masses of the ferrous and ferric ions.

If the alkaline carbonate employed is only slightly in excess of that required to precipitate the copper and iron salts, the concentration of the carbonic acid ions will be greatly diminished. Under these more favorable conditions reduction slowly takes place with loss of carbon dioxide. The carbonates gradually change to a brick-red precipitate containing metallic copper and basic ferric carbonate.

As is well known, the acid ferrous and cupric carbonates are more soluble than the corresponding normal or basic salts of these metals. The influence of this greater solubility is shown in the precipitation of small amounts of copper even in the presence of a large excess of alkaline bicarbonates. If the metallic chlorides are added to a saturated solution of acid potassium carbonate and the mixture allowed to stand for twenty-four hours, a slight film of metallic copper, mixed with basic ferric carbonate, is deposited on the walls of the vessel.

The solubility of the acid carbonates of iron and copper is largely increased under pressure.[2] The greater concentration of the metallic ions thus obtained produces a ready reduction of copper even in the presence of concentrated solutions of the acid alkaline carbonates.

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[1] E. Braun : *Loc. cit.*

[2] R. Wagner : Ztschr. anal. Chem., **6**, 167.

A tube containing a solution of ferrous and cupric chlorides is placed in a thick-walled flask holding a saturated solution of potassium bicarbonate. The flask is then filled with carbon dioxide, tightly sealed, and the contents of the tube mixed with the alkaline bicarbonate. The precipitate formed gradually loses carbonic acid, finally assuming the brick-red color already noted. The supernatant ruddy liquid owes its color to the presence of some basic ferric carbonate, which is deposited when the solution is warmed, as ferric hydroxide. The precipitate contains finely divided copper, which cannot readily be freed from the intimately associated ferric iron by treatment with hydrochloric acid, because of the solvent action of ferric chloride, but on digesting the original mixture a short time a coagulum is usually formed, from which, by repeated agitation with water, the heavier metal is separated.

The copper thus obtained is of characteristic appearance, is insoluble in hydrochloric acid, but soluble in nitric, the solution showing the presence of copper and absence of iron.

The reduction of copper from the cuprous condition may be effected in the same manner as from the cupric. This is readily shown by substituting for the cupric salt, in the above reaction, cuprous chloride dissolved in a solution of sodium chloride. From one gram of cuprous chloride more than half of the metal can thus be easily isolated as pure copper, free from ferric iron.

UNIVERSITY OF CHICAGO.

OBITUARY.

WALDRON SHAPLEIGH.

On the 30th of August died Mr. Waldron Shapleigh. Mr. Shapleigh had been connected with the Welsbach Light Company from its beginning, as its chemist, and was very well known in scientific circles as perhaps the best authority living on the properties of rare earths.

Mr. Shapleigh began his life of manly independence at an unusually early age. He decided against a college course, and studied chemistry under the late Professor Williams. At the age of nineteen he was made Superintendent of the Blair County, Pa., Zinc Works, and a year later accepted a position as Instructor of Chemistry at Lehigh University. He remained there several years, at the last filling the place and receiving the salary of Professor Wetherill, after the latter's death. Determining to enter a different field of chemistry, Mr. Shapleigh severed his connection with the University and went to France to study the beet-root sugar industry. He remained there nearly two years, and upon his return was engaged as chemist by the Kings County Sugar Refinery, New York, then engaged in the manufacture of glucose. Mr. Shapleigh remained with this company for ten years, until its dissolution. He next entered the Welsbach Company, when it was founded as an industry, and it is through his connection with it that he became so widely known in scientific circles, both in Europe and America.

Mr. Shapleigh was chosen as one of the judges of awards in the chemical section at the Columbian Fair in 1893, and his exhibitions of rare earths at different expositions have always received medals.

Mr. Shapleigh was a man of unusual character; in an age of greed to be rich he kept before him a certain simply strenuous ideal of high old-fashioned honor from which he never departed. He was a rare combination of strength and gentleness, impressing every one who knew him with deep respect. By those friends who could pierce the armor of shy reserve which hedged him about, he was deeply loved and deeply lamented. He leaves a widow, a son, and a daughter.—*N. Y. Evening Post.*

NOTE.

The Dissociating Power of Hydrogen Sulphide.

In view of the analogous behavior, in many respects, of oxygen and sulphur, it would seem quite probable that hydrogen sulphide in the liquid state should possess, in common with water, the property of ionizing substances in solution.

It is more difficult to experiment with hydrogen sulphide than with liquid ammonia, which has recently been so thoroughly tested in this respect, on account of the difficulty of reducing it to the liquid state.

The liquefaction of sufficient gas to serve as an electrolyte was accomplished at room temperature in a Pictet compression apparatus, some grains of potassium chloride having been previously placed in the tube. The column of mercury within the tube served as one electrode, and a platinum wire, sealed into the top of the tube, as the other.

The salt readily went into solution when the liquid collected in the tube, but, on making electric connections, there did not appear to be any conduction.

The liquid exerted considerable action upon the mercury surface, and, fearing that this coating of sulphide might form an insulating layer, two platinum electrodes were used, but with a negative result again. The galvanometer in the circuit, a fairly sensitive one of the Wheatstone type, did not show any deflection, even when a battery of 40 volts was used.

An attempt to use an iron wire as electrode showed a most vigorous chemical action upon the iron. WM. T. SKILLING.

UNIV. OF CALIFORNIA,
July 4, 1901.

REVIEWS.

LECTURES ON THE HISTORY OF THE DEVELOPMENT OF CHEMISTRY SINCE THE TIME OF LAVOISIER. By DR. A. LADENBURG. Translated from the second German edition by LEONARD DOBBIN, PH.D., with additions and corrections by the author. Edinburgh: Published by the Alembic Club. Edinburgh Agent: William F. Clay. pp. xvi + 373. Price, 6s. 6d.

There are two views of history. One regards it merely as a record of events. The other regards every event as closely dependent on what has gone before and closely related to what follows, and concerns itself with tracing the sequence which always exists. It is evidently this latter view which is dominant with Professor Ladenburg as he writes. The first German edition of the book was published thirty years ago; the second, and last, fifteen years ago, but an additional chapter has been prepared for use in this translation, bringing the material very closely down to date.

The picture which is given of the growth of chemical science from the time of Lavoisier down through the first two-thirds of the nineteenth century is very clear and satisfactory. Up to, and including the development of structural organic chemistry, it has been possible to bring out the various factors which have contributed to the development of our knowledge in bold relief and proper relation. The author has performed a very difficult task in a most excellent manner.

The historian of the progress of the last thirty years meets with a two-fold difficulty. The science has become vastly more complex, and the number of workers is greatly increased, giving a wealth of material that no one can grasp in its entirety. And the period is so close to our own time that it is impossible to separate the permanent from that which is ephemeral. For this reason the chapters dealing with this period consist chiefly of a series of very brief statements about a multitude of new discoveries, and that clear, logical arrangement, which characterizes the earlier portions of the book, has been impossible.

The value of the book is greatly increased by more than a thousand references to original papers. These will make it easy, for those who wish, to follow in greater detail the topics which are discussed.

Only very rarely are to be found sentences written fifteen or thirty years ago which need some change in the light of present knowledge. No one would now contend, as is implied on page 270, that the unsaturated acids studied by Fittig in the seventies contain bivalent carbon atoms. And it is, perhaps, too much to ask that Ladenburg should give the facts which demonstrate that his prism formula for benzene is false.

The translation is excellent throughout. W. A. N.

PRACTICAL ELECTROCHEMISTRY. By BERTRAM BLOUNT. Westminster: Archibald, Constable & Co., Ltd. New York: The Macmillan Co. 1901. pp. xii + 374. Price 15s.

This book consists, chiefly, of a description of practical processes which are in actual commercial use. Only the first thirty pages are given to a discussion of general principles. While a fairly clear general statement of the theory of solutions is given, the attitude of the author in the matter is indicated by the following sentences: "This conception is a mode of thought and not an objective reality, and may eventually be replaced by a hypothesis involving fewer and less sweeping assumptions. * * * * Fortunately all practical applications of electrolysis can be satisfactorily considered without having recourse to this hypothesis, and the practician who is equipped with a sound knowledge of the principles of chemistry and electricity can grapple successfully with any problem in electrolysis which is likely to present itself, irrespective of the precise explanation which may be at the moment most agreeable with the teachings of the ionic hypothesis." Such a statement may be essentially true so far as the present development of technical electrochemistry is concerned, but that it will long remain true, no one acquainted with the achievements of the theory along purely scientific lines, will believe.

The technical processes considered in the book are: Winning and refining of metals by electrolysis in aqueous and in igneous solutions; winning and refining metals and their alloys in the electric furnace—carbides, borides, and silicides; electro-deposition; alkali, chlorine, and their products; electrolytic manufacture of organic compounds and fine chemicals; and power. What the book lacks from the theoretical standpoint is very largely compensated by the careful descriptions given of methods in actual use, with details of the materials and products obtained, and of the voltages and energy required.

The value of the book would be increased by the introduction of a few tables of physical constants. W. A. N.

THE ELEMENTARY PRINCIPLES OF CHEMISTRY. BY A. V. E. YOUNG, Professor of Chemistry in Northwestern University. New York: D. Appleton & Co. 1901. Part I: pp. 252 + xiv; Part II: pp. 106. SUGGESTIONS TO TEACHERS DESIGNED TO ACCOMPANY THE ELEMENTARY PRINCIPLES OF CHEMISTRY. Pp. 48.

This is a scholarly book. The author is a strong advocate of the value of the quantitative method in an elementary course and in preparing his book he has had this constantly in mind. He says: "The quantitative method aims to bring the student into direct contact, so to speak, with the relations of quantity as well as with those of quality. It most distinctly does not aim to present the systematic methods of quantitative analysis. No more does it propose that the pupil shall prove to his own mind the laws of quantity. Such laws are inductions from a great many observations, and the student should be carefully guarded against the idea that his experiments are to prove them, even to his own conviction. His experimentation is simply to aid him by direct observation and by guided thought to get a clear notion of the content and meaning of laws."

The first seven chapters (89 pages) of the book have to deal with the following subjects:

I. Matter, Energy, Substances, Chemical Properties, Physical Properties.

II. The Fundamental Quantitative Laws of Chemical Changes.

III. Combining Weights, Notation, Equations, Stoichiometry, Nomenclature.

IV. Relation between Volume, Pressure, and Temperature of Gases.

V. The Relation between Equivalent and Combining Weights and Certain Specific Properties.

VI. Method of Determining Equivalent and Combining Weights of Elements and Formulas of Compounds.

VII. The Atomic Theory.

As will be seen, the student has been occupied up to this time with the study of the great fundamental laws of chemistry and some of its most important theories, and his laboratory work has had for its object the illustration and emphasizing of these laws and theories. Now in Chapter VIII, which deals with the "Relation between the Properties of the Elements in General and their Combining Weights," he begins a systematic, though necessarily brief, study of the important elements and their principal compounds. This chapter occupies about 150 pages. It is clearly written and the material is wisely selected. The book deserves a careful examination. Whether it is better adapted to the needs of the beginner than other books now in use can only be determined by experiment.

THE HISTORY OF THE DEVELOPMENT OF THE MANUFACTURE OF INDIGO. By H. BRUNCK, PH.D.

This is a good English translation of the remarkable address of H. Brunck, Managing Director of the Badische Anilin- und Soda-Fabrik, delivered October 20, 1900, on the occasion of the Dedication of the Hofmann Memorial in Berlin, erected in honor of A. W. von Hofmann by the chemists of all nations. It has been prepared and presented to their friends and patrons by Messrs. Kuttroff, Pickhardt & Co., of New York. As the address was published in full in the *Berichte* and has been republished elsewhere, it is not necessary to go into detail in regard to it here. Suffice it to say that in the opinion of the present writer it is one of the most interesting addresses ever presented to chemists. This beautifully prepared pamphlet gives it a worthy setting. Every chemist, whether "inorganic," "organic," "physical," "analytical," "industrial," or just plain chemist, will do well not only to read the address but to study it. I. R.

AN INTRODUCTION TO THE STUDY OF CHEMISTRY. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. Sixth edition. Revised and enlarged. New York: Henry Holt and Company. 1901. pp. 460 + xxii.

The preface will serve to give an idea of the general character of this revised edition: "Since the appearance of the last edition of this book many important discoveries have been made in chemistry. In preparing the new edition the author has endeavored to include all discoveries that come within the scope of the book, and it is believed that nothing that could fairly be looked for in a book of this size has been omitted. The experiments have not been essentially changed. The question whether it is advisable to introduce a larger number of quantitative experiments was fully considered. The conclusion reached was that in the time generally available, it would be impossible properly to perform a larger number of such experiments than is described in the earlier editions. That has been our experience in our first year's course, and it has been the experience of many teachers who have kindly given the author the benefit of their advice.

"Some account of the new theory of solutions is given, and its application to the explanation of reactions that take place in water solutions receives consideration. It would, of course, be an easy matter to go further into the subject, but it does not seem to the author wise to do so in the earliest stages of the study of chemistry."

A TEXT-BOOK OF URINE ANALYSIS FOR STUDENTS AND PRACTITIONERS OF MEDICINE. By JOHN H. LONG, M.S., SC.D. With numerous illustrations. Easton, Pa.: THE Chemical Publishing Co. 1900. pp. vi + 249. Price $1.50.

The experience of the author, both as a professor in a medical school and as a practical analyst, as well as his own researches in the field of urine analysis, have given him an unusually thorough preparation for the writing of a book on this subject. The result is a work excellently adapted for practical use. While the book is comprehensive in its scope, giving a considerable number of qualitative tests and of quantitative methods for determining the more important constituents of the urine, the claim of the author that methods of doubtful utility are consistently excluded is well sustained.

Not only is the book well written from the chemical standpoint, but clear statements of the clinical significance of the various substances discussed supply the need of the medical practitioner. Careful directions for the microscopical examination of sediments are included, and these are supplemented by a sufficient number of figures illustrating the substances to be looked for.

An appendix gives the necessary tables, directions for the preparation of reagents, and an excellent tabular statement of the clinical significance of the results of analysis, and also, in detail, the character of the urine to be expected in eight important diseases.
W. A. N.

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Contributions from the Sheffield Laboratory of Yale University.

LXXXVII.—GENERALIZATIONS ON DOUBLE HALOGEN SALTS.

BY H. L. WELLS.

The object of this communication is to point out some conclusions in regard to double halides in general. For this purpose a rather full list of these compounds has been prepared. This list is not supposed to be complete, for the literature has not been searched with care except in the cases of certain series which have been studied in this laboratory,[1] but it is believed to be sufficiently complete for the purpose in view. Care has been taken to consult the original articles where salts of unusual composition have been described, and a few of these have been discarded on account of evidence that they were not real compounds, but no double salt has been rejected simply because it appeared to be irregular.

It has been thought best to limit the present discussion to the salts of the alkali metals, ammonium, and univalent thallium; for, to include the double halides of the organic bases and those in which bivalent metals form the more positive halides, would greatly enlarge the list, probably without giving any additional insight into the nature of the compounds.

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[1] See Am. J. Sci. from 1892 to the present time. References are given beyond to most of these articles, but reference to general literature is not attempted.

For convenience, the double salts will be arranged according to types, which will be designated by ratios indicating the number of atoms of the two metals; thus, $KCl.SnCl_2$ is a 1 : 1 salt; $2KCl.PtCl_4$ is a 2 : 1 salt; and $CsCl.2PbCl_2$ is a 1 : 2 salt. The number referring to the atoms of alkali metal, etc., will be invariably placed first.

I. SALTS OF UNIVALENT NEGATIVE METALS.

Cuprous Salts.[1]

3 : 1	2 : 1	3 : 2
$3CsCl.CuCl.H_2O$	$2NH_4Cl.CuCl$ $2NH_4Br.CuBr$ $2KCl.CuCl$	$3CsCl.2CuCl$

1 : 1	2 : 3	1 : 2
$NH_4Cl.CuCl$ $NH_4Br.CuBr$ $NH_4I.CuI.H_2O$.	$2NH_4Cl.3CuCl$	$CsCl.2CuCl$

Silver and Aurous Salts.[2]

2 : 1	1 : 1
$2KI.AgI$ $2RbI.AgI$ $2CsI.AgI$	$NH_4Cl.AgCl$ $KCl.AgCl$ $KI.AgI$ $KCl.AuCl$

II. SALTS OF BIVALENT NEGATIVE METALS.

Beryllium Salts.

2 : 1	1 : 1
$2KF.BeF_2$ $2KCl.BeCl_2$	$KF.BeF_2$

Magnesium Salts.[3]

1 : 1

$NH_4Cl.MgCl_2.6H_2O$
$NH_4Br.MgBr_2.6H_2O$
$NH_4I.MgI_2.6H_2O$
$NaF.MgF_2$
$NaCl.MgCl_2.H_2O$
$KCl.MgCl_2.6H_2O$
$KBr.MgBr_2.6H_2O$
$KI.MgI_2.6H_2O$
$RbCl.MgCl_2.6H_2O$
$CoCl.MgCl_2.6H_2O$
$CsBr.MgBr_2.6H_2O$

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[1] Am. J. Sci., (3), 47, 96.

[2] *Ibid.*, (3), 44, 155, 157.

[3] Wells and Campbell: *Ibid.*, (3), 46, 431.

Manganese Salts.[1]

2 : 1	1 : 1
$2NH_4Cl.MnCl_2.2H_2O$	$NH_4Cl.MnCl_2.2H_2O$
$2RbCl.MnCl_2.2H_2O$	$KCl.MnCl_2.2H_2O$
$2CsCl.MnCl_2.2H_2O$	$CsCl.MnCl_2.2H_2O$

Ferrous and Nickel Salts.

2 : 1	1 : 1
$2NH_4Cl.FeCl_2$	$KF.FeF_2.H_2O$
$2KF.FeF_2$	$NH_4Cl.NiCl_2.6H_2O$
$2KCl.FeCl_2.2H_2O$	$NaF.NiF_2.H_2O$
$2NH_4F.NiF_2.2H_2O$	$KF.NiF_2.H_2O$
$2KF.NiF_2$	$CsCl.NiCl_2$
	$CsBr.NiBr_2$

Cobalt Salts.[2]

3 : 1	2 : 1	1 : 1
$3CsCl.CoCl_2$	$2NH_4F.CoF_2.2H_2O$	$NH_4Cl.CoCl_2.6H_2O$
$3CsBr.CoBr_2$	$2CsCl.CoCl_2$	$NaF.CoF_2.H_2O$
	$2CsBr.CoBr_2$	$KF.CoF_2.H_2O$
	$2CsI.CoI_2$	$CsCl.CoCl_2.2H_2O$

Cupric Salts.[3]

2 : 1	3 : 2
$2NH_4F.CuF_2.2H_2O$	$3CsCl.2CuCl_2.2H_2O$
$2NH_4Cl.CuCl_2.2H_2O$	
$2NH_4Br.CuBr_2.2H_2O$	
$2KF.CuF_2$	
$2KCl.CuCl_2$	
$2CsCl.CuCl_2$	
$2CsCl.CuCl_2.2H_2O$	
$2CsBr.CuBr_2$	

1 : 1	
$NH_4F.CuF_2.2\frac{1}{2}H_2O$	$RbF.CuF_2$
$NH_4Cl.CuCl_2.2H_2O$	$CsCl.CuCl_2$
$LiCl.CuCl_2.2H_2O$	$CsBr.CuBr_2$
$KF.CuF_2$	

[1] Saunders: This JOURNAL, 14, 152.

[2] Campbell: Am. J. Sci., (3), 48, 418.

[3] Wells and Dupee: *Ibid.*, (3), 47, 91.

Zinc Salts.[1]

4 : 1

$4NH_4Cl.ZnCl_2$

3 : 1

$3NH_4Cl.ZnCl_2$
$3CsCl.ZnCl_2$
$3CsBr.ZnBr_2$
$3CsI.ZnI_2$

2 : 1

$2NH_4F.ZnF_2.2H_2O$
$2NH_4Cl.ZnCl_2$
$2NH_4Cl.ZnCl_2.H_2O$
$2NH_4Br.ZnBr_2$
$2NH_4I.ZnI_2$
$2NaCl.ZnCl_2.3H_2O$
$2NaI.ZnI_2.3H_2O$
$2KF.ZnF_2$
$2KCl.ZnCl_2$
$2KI.ZnI_2$
$2CsCl.ZnCl_2$
$2CsBr.ZnBr_2$
$2CsI.ZnI_2$

1 : 1

$NH_4Cl.ZnCl_2.2H_2O$
$NaF.ZnF_2$
$NaI.ZnI_2.3H_2O$
$KF.ZnF_2$
$KI.ZnI_2$

Cadmium Salts.[2]

4 : 1

$4NH_4Cl.CdCl_2$
$4NH_4Br.CdBr_2$
$4KCl.CdCl_2$
$4KBr.CdBr_2$

3 : 1

$3CsBr.CdBr_2$
$3CsI.CdI_2$

2 : 1

$2NH_4Cl.CdCl_2$
$2NH_4Cl.CdCl_2.H_2O$
$2NH_4Br.CdBr_2.\frac{1}{2}H_2O$
$2NH_4I.CdI_2.2H_2O$
$2NaCl.CdCl_2.3H_2O$
$2NaBr.CdBr_2.5H_2O$
$2NaI.CdI_2.6H_2O$
$2KCl.CdCl_2$
$2KCl.CdCl_2.H_2O$
$2KBr.CdBr_2$
$2KI.CdI_2.2H_2O$
$2CsCl.CdCl_2$
$2CsBr.CdBr_2$
$2CsI.CdI_2$

1 : 1

$NH_4F.CdF_2$
$NH_4Br.CdBr_2.\frac{1}{2}H_2O$
$NaBr.CdBr_2.2\frac{1}{2}H_2O$
$KCl.CdCl_2$
$KCl.CdCl_2.\frac{1}{2}H_2O$
$KBr.CdBr_2.\frac{1}{2}H_2O$
$KI.CdI_2.H_2O$
$CsCl.CdCl_2$
$CsBr.CdBr_2$
$CsI.CdI_2$

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[1] Wells and Campbell: Am. J. Sci., (3), **46**, 431.

[2] Wells and Walden: *Ibid.*, (3), **46**, 425.

Stannous Salts.

4 : 1

$4NH_4Cl.SnCl_2.3H_2O$
$4KCl.SnCl_2.3H_2O$

2 : 1

$2NH_4F.SnF_2.2H_2O$
$2NH_4Cl.SnCl_2.H_2O$

1 : 1

$NH_4I.SnI_2$
$NH_4I.SnI_2.1\frac{1}{2}H_2O$
$NaI.SnI_2$
$KI.SnI_2.1\frac{1}{2}H_2O$

2 : 3

$2NaF.3SnF_2$
$2KF.3SnF_2.H_2O$

Mercuric Salts.[2]

3 : 1

$3CsCl.HgCl_2$
$3CsBr.HgBr_2$
$3CsI.HgI_2$

2 : 1

$2NH_4Cl.HgCl_2.H_2O$
$2NH_4Br.HgBr_2$
$2NH_4I.HgI_2.3H_2O$
$2NaCl.HgCl_2$
$2NaI.HgI_2$
$2KCl.HgCl_2.H_2O$
$2KBr.HgBr_2$
$2KI.HgI_2$
$2RbCl.HgCl_2$
$2RbCl.HgCl_2.2H_2O$
$2CsCl.HgCl_2$
$2CsBr.HgBr_2$
$2CsI.HgI_2$

1 : 1

$NH_4Cl.HgCl_2$
$NH_4Cl.HgCl_2.H_2O$
$NH_4Br.HgBr_2$
$NH_4I.HgI_2.H_2O$
$LiCl.HgCl_2$
$NaCl.HgCl_2.1\frac{1}{2}H_2O$
$NaBr.HgBr_2$
$NaI.HgI_2.1\frac{1}{2}H_2O$
$KCl.HgCl_2$
$KCl.HgCl_2.H_2O$
$KBr.HgBr_2$
$KBr.HgBr_2.H_2O$
$KI.HgI_2.1\frac{1}{2}H_2O$
$RbCl.HgCl_2$
$CsCl.HgCl_2$
$CsBr.HgBr_2$
$CsI.HgI_2$
$TlCl.HgCl_2$

2 : 3

$2NH_4Cl.3HgCl_2.4H_2O$
$2CsI.3HgI_2$

---

[1] Am. J. Sci., (3), 44, 221.

1 : 2

$KCl.2HgCl_2.2H_2O$
$RbCl.2HgCl_2$
$CsCl.2HgCl_2$
$CsBr.2HgBr_2$
$CsI.2HgI_2$

1 : 5

$NH_4Cl.5HgCl_2$
$CsCl.5HgCl_2$

Palladious, Platinous, and Iridious Salts.

2 : 1

$2NH_4Cl.PdCl_2$
$2NH_4Cl.PtCl_2$
$2NH_4I.IrI_2$
$2NaCl.PdCl_2$
$2NaCl.PtCl_2.4H_2O$
$2KCl.PdCl_2$
$2KCl.PtCl_2$
$2KBr.PtBr_2$
$2CsCl.PdCl_2$
$2CsCl.PtCl_2$

1 : 1

$LiCl.PtCl_2.6H_2O$
$KCl.PdCl_2$
$KCl.PtCl_2$
$RbCl.PtCl_2$

Lead Salts.[1]

4 : 1

$4CsCl.PbCl_2$
$4CsBr.PbBr_2$

2 : 1

$2NH_4Br.PbBr_2.H_2O$
$2KBr.PbBr_2.H_2O$
$2RbCl.PbCl_2.\frac{1}{2}H_2O$
$2RbBr.PbBr_2.\frac{1}{2}H_2O$

1 : 1

$NH_4Cl.PbCl_2.\frac{1}{3}H_2O$
$NH_4I.PbI_2.2H_2O$
$KCl.PbCl_2.\frac{1}{3}H_2O$
$KBr.PbBr_2.\frac{1}{3}H_2O$
$KBr.PbBr_2.H_2O$
$KI.PbI_2.2H_2O$
$RbI.PbI_2.2H_2O$
$CsCl.PbCl_2$
$CsBr.PbBr_2$
$CsI.PbI_2$

1 : 2

$NH_4Cl.2PbCl_2$
$NH_4Br.2PbBr_2$
$KCl.2PbCl_2$
$KBr.2PbBr_2$
$RbCl.2PbCl_2$
$RbBr.2PbBr_2$
$CsCl.2PbCl_2$
$CsBr.2PbBr_2$

III. SALTS OF TRIVALENT NEGATIVE METALS.

Aluminium Salts.

3 : 1

$3NH_4F.AlF_3$
$3NaF.AlF_3$
$3KF.AlF_3$

2 : 1

$2NaF.AlF_3$
$2KF.AlF_3$

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[1] Nearly all the older work on double halides of lead was entirely erroneous. See Remsen and Herty: This JOURNAL, **14**, 107; Wells: Am. J. Sci., (3), **45**, 121; Wells and Johnson: *Ibid.*, **46**, 25, 34.

3 : 2	1 : 1
$3NaF.2AlF_3$[1]	$NaCl.AlCl_3$
	$KCl.AlCl_3$
	$KBr.AlBr_3$
	$KI.AlI_3$

Vanadium Salts.

3 : 1	5 : 2
$3NH_4F.VF_3$	$5NaF.2VF_3.H_2O$

2 : 1	1 : 1
$2NH_4F.VF_3.H_2O$	$NH_4F.VF_3.2H_2O$
$2KF.VF_3.H_2O$	

Chromium Salts.[2]

3 : 1	2 : 1	1 : 1
$3NH_4F.CrF_3$	$2NH_4F.CrF_3.H_2O$	$KCl.CrCl_3$
$3KF.CrF_3$	$2NH_4Cl.CrCl_3.H_2O$	
$3KCl.CrCl_3$	$2NaF.CrF_3.H_2O$	
$3TlCl.CrCl_3$	$2KF.CrF_3.H_2O$	
	$2KCl.CrCl_3.2H_2O$	
	$2CsCl.CrCl_3.H_2O$	
	$2CsCl.CrCl_3.4H_2O$	

Titanous and Manganic Salts.

3 : 1	2 : 1
$3NH_4F.TiF_3$	$2NH_4F.MnF_3$
	$2NaF.MnF_3$
	$2KF.MnF_3$
	$2NH_4F.TiF_3$

Ferric Salts.[3]

3 : 1	2 : 1
$3NH_4F.FeF_3$	$2NH_4F.FeF_3$
$3KF.FeF_3$	$2NH_4Cl.FeCl_3$
$3CsCl.FeCl_3.H_2O$	$2NaF.FeF_3.\frac{1}{2}H_2O$
$3TlCl.FeCl_3$.	$2NaCl.FeCl_3.H_2O$
	$2KF.FeF_3$
	$2KCl.FeCl_3.H_2O$
	$2RbCl.FeCl_3.H_2O$
	$2RbBr.FeBr_3.H_2O$
	$2CsCl.FeCl_3.H_2O$
	$2CsBr.FeBr_3.H_2O$

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[1] The formula for chiolite is somewhat doubtful. Some authorities prefer the formula $5NaF.3AlF_3$, but the simpler formula is selected here.

[2] Wells and Boltwood: Am. J. Sci., (3), 50, 249.

[3] Walden: *Ibid.*, (3), 48, 283.

1 : 1

$NH_4Br.FeBr_3.2H_2O$
$CsCl.FeCl_3$
$CsBr.FeBr_3$

Arsenious Salts.[1]

3 : 2

$3RbCl.2AsCl_3$
$3RbBr.2AsBr_3$
$3RbI.2AsI_3$

$3CsCl.2AsCl_3$
$3CsBr.2AsBr_3$
$3CsI.2AsI_3$

Indium Salts.

3 : 1

$3KCl.InCl_3.1\frac{1}{2}H_2O$

2 : 1

$2NH_4Cl.InCl_3.H_2O$

Antimonious Salts.[2]

4 : 1

$4NH_4I.SbI_3.3H_2O$

3 : 1

$3NH_4Cl.SbCl_3.1\frac{1}{2}H_2O$
$3NaF.SbF_3$
$3NaCl.SbCl_3$

7 : 3

$7KCl.3SbCl_3$
$7KBr.3SbBr_3.8H_2O$
$7RbCl.3SbCl_3$
$7RbBr.3SbBr_3$

2 : 1

$2NH_4F.SbF_3$
$2NH_4Cl.SbCl_3$
$2NH_4Cl.SbCl_3.H_2O$
$2LiF.SbF_3$
$2KF.SbF_3$
$2KCl.SbCl_3$
$2KCl.SbCl_3.2H_2O$
$2CsF.SbF_3$

3 : 2

$3NH_4I.2SbI_3.3H_2O$
$3NaI.2SbI_3.12H_2O$
$3KI.2SbI_3.3H_2O$
$3RbCl.2SbCl_3$
$3RbBr.2SbBr_3$
$3RbI.2SbI_3$
$3CsCl.2SbCl_3$
$3CsI.2SbI_3$

1 : 1

$NH_4Cl.SbCl_3$
$NH_4I.SbI_3.2H_2O$
$KF.SbF_3$
$KI.SbI_3.H_2O$
$RbCl.SbCl_3$
$CsF.SbF_3$

3 : 4

$3NH_4I.4SbI_3.9H_2O$

4 : 7

$4CsF.7SbF_3$

1 : 2

$RbCl.2SbCl_3$
$CsF.2SbF_3$

1 : 3

$CsF.3SbF_3$

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[1] Wheeler: Am. J. Sci., (3), **46**, 88.

[2] Wheeler: *Ibid.*, (3), **46**, 269; Wells and Metzger: *Ibid.*, (4), **11**, 451.

Auric Salts.[1]

1 : 1

$NH_4Cl.AuCl_3.H_2O$
$NH_4Cl.AuCl_3.2\frac{1}{2}H_2O$
$NaCl.AuCl_3.2H_2O$
$NaBr.AuBr_3.2H_2O$
$KCl.AuCl_3.\frac{1}{2}H_2O$
$KCl.AuCl_3.2H_2O$
$KBr.AuBr_3.2H_2O$
$KI.AuI_3$
$RbCl.AuCl_3$
$RbBr.AuBr_3$
$CsCl.AuCl_3$
$CsCl.AuCl_3.\frac{1}{2}H_2O$
$CsBr.AuBr_3$
$TlCl.AuCl_3$

Rhodium, Ruthenium, Indium, and Osmium Salts.

3 : 1

$3NH_4Cl.RhCl_3.1\frac{1}{2}H_2O$
$3NH_4Cl.IrCl_3.1\frac{1}{2}H_2O$
$3NH_4Br.IrBr_3.\frac{1}{2}H_2O$
$3NH_4I.IrI_3.\frac{1}{2}H_2O$
$3NaCl.RhCl_3.9H_2O$
$3NaCl.IrCl_3.12H_2O$
$3NaBr.IrBr_3.\frac{1}{2}H_2O$
$3KCl.RhCl_3$
$3KCl.IrCl_3.3H_2O$
$3KBr.IrBr_3.3H_2O$
$3KI.IrI_3$
$3KCl.OsCl_3.6H_2O$

2 : 1

$2NH_4Cl.RhCl_3.H_2O$
$2NH_4Cl.RuCl_3$
$2NH_4Cl.OsCl_3.1\frac{1}{2}H_2O$
$2KCl.RhCl_3.H_2O$
$2KCl.RhCl_3.3H_2O$
$2KCl.RuCl_3$

Bismuth Salts.

4 : 1

$4NH_4Cl.BiCl_3$
$4KI.BiI_3$

3 : 1

$3NH_4Cl.BiCl_3$
$3NaCl.BiCl_3$
$3KCl.BiCl_3$
$3KI.BiCl_3$
$3RbCl.BiCl_3$
$3CsCl.BiCl_3$

7 : 3

$7RbCl.3BiCl_3$

2 : 1

$2NH_4Cl.BiCl_3$
$2NaCl.BiCl_3.3H_2O$
$2KCl.BiCl_3.2H_2O$
$2KI.BiI_3.H_2O$

3 : 2

$3NaI.2BiI_3$
$3KCl.2BiCl_3$
$3CsCl.2BiCl_3$

1 : 1

$NH_4Cl.BiCl_3$
$KCl.BiCl_3.H_2O$
$KI.BiI_3$
$RbCl.BiCl_3.H_2O$

1 : 2

$NH_4Cl.2BiCl_3$

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[1] Wells and Wheeler : Am. J. Sci., (3), 44, 157.

Thallic Salts.[1]

5 : 1

$5TlI.TlI_3$

3 : 1

$3NH_4Cl.TlCl_3.2H_2O$
$3NH_4Cl.TlCl_3$
$3NH_4I.TlI_3$
$3LiCl.TlCl_3.8H_2O$
$3NaCl.TlCl_3.12H_2O$
$3KCl.TlCl_3.2H_2O$
$3RbCl.TlCl_3.H_2O$
$3RbBr.TlBr_3.H_2O$
$3CsCl.TlCl_3.H_2O$
$3TlCl.TlCl_3$
$3TlBr.TlBr_3$

2 : 1

$2KCl.TlCl_3.2H_2O$
$2RbCl.TlCl_3.H_2O$
$2CsCl.TlCl_3$
$2CsCl.TlCl_3.H_2O$

3 : 2

$3KCl.2TlCl_3.1\frac{1}{2}H_2O$
$3KBr.2TlBr_3.3H_2O$
$3KI.TlI_3.3H_2O$
$3CsCl.2TlCl_3$
$3CsBr.2TlBr_3$

1 : 1

$NH_4Br.TlBr_3.2H_2O$
$NH_4Br.TlBr_3.4H_2O$
$NH_4Br.TlBr_3$
$NH_4I.TlI_3$
$KBr.TlBr_3$
$KI.TlI_3$
$RbBr.TlBr_3$
$RbI.TlI_3$
$CsBr.TlBr_3$
$CsI.TlI_3$
$TlCl.TlCl_3$
$TlBr.TlBr_3$

IV. SALTS OF QUADRIVALENT NEGATIVE METALS.

Titanic,[2] *Germanium, and Manganese Salts.*

2 : 1

$2NH_4F.TiF_4$
$2NaF.TiF_4$
$2KF.TiF_4.H_2O$

$2RbF.TiF_4$
$2KF.MnF_4$
$2KF.GeF_4$

Zirconium Salts.[3]

4 : 1

$4LiF.ZrF_4.\frac{2}{3}H_2O$

3 : 1

$3NH_4F.ZrF_4$
$3KF.ZrF_4$

5 : 2

$5NaF.2ZrF_4$

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[1] Pratt: Am. J. Sci., (3), 49, 397.

[2] Rose's compounds, $6NH_4Cl.TiCl_4$ and $3NH_4Cl.TiCl_4$, are omitted here because they represent sublimates of variable composition. Pennington's salt, $4CsF.TiF_4$, is also left out, as it was described with two other caesium salts of very suspicious composition, which are referred to under the pentavalent compounds.

[3] Wells and Foote: *Ibid.*, (4), 1, 18; 3, 466.

2 : 1
$2NH_4F.ZrF_4$
$2LiF.ZrF_4$
$2NaF.ZrF_4$
$2NaCl.ZrCl_4$
$2KF.ZrF_4$
$2CsF.ZrF_4$

5 : 3
$5TlF.3ZrF_4$

1 : 1
$KF.ZrF_4.H_2O$
$CsF.ZrF_4$
$TlF.ZrF_4$
$TlF.ZrF_4.H_2O$

2 : 3
$2CsF.3ZrF_4.2H_2O$

Stannic and Antimony Salts.

4 : 1
$4NH_4F.SnF_4$

2 : 1
$2NH_4Cl.SnCl_4$
$2LiF.SnF_4.2H_2O$
$2NaF.SnF_4$
$2NaCl.SnCl_4$
$2NaCl.SnCl_4.6H_2O$
$2NaBr.SnBr_4.6H_2O$

$2KF.SnF_4.H_2O$
$2KCl.SnCl_4$
$2RbCl.SnCl_4$
$2CsCl.SnCl_4$
$2CsCl.SbCl_4$

Tellurium Salts.[1]

2 : 1
$2KCl.TeCl_4$
$2KBr.TeBr_4.2H_2O$
$2KI.TeI_4.2H_2O$
$2RbCl.TeCl_4$
$2RbBr.TeBr_4$

$2RbI.TeI_4$
$2CsCl.TeCl_4$
$2CsBr.TeBr_4$
$2CsI.TeI_4$

1 : 1
$NH_4F.TeF_4$
$KF.TeF_4$
$CsF.TeF_4$

Ceric Salt.

3 : 2
$3KF.CeF_4.2H_2O$

Platinum Group Salts.

2 : 1
$2NH_4Cl.PdCl_4$
$2NH_4Cl.RuCl_4$
$2NH_4Cl.IrCl_4$
$2NH_4Cl.PtCl_4$
$2NH_4Cl.OsCl_4$
$2NH_4Br.PtBr_4$
$2NH_4Br.IrBr_4$
$2NH_4I.PtI_4$
$2LiCl.PtCl_4.6H_2O$
$2NaCl.PtCl_4.6H_2O$

$2NaCl.IrCl_4.6H_2O$
$2NaCl.OsCl_4$
$2NaBr.IrBr_4$
$2NaI.PtI_4.6H_2O$
$2NaI.IrI_4$
$2KCl.PdCl_4$
$2KCl.RuCl_4$
$2KCl.PtCl_4$
$2KCl.IrCl_4$

$2KCl.OsCl_4$
$2KBr.PdBr_4$
$2KBr.PtBr_4$
$2KBr.IrBr_4$
$2KI.PtI_4$
$2KI.IrI_4$
$2RbCl.PtCl_4$
$2CsCl.PtCl_4$
$2TlCl.PtCl_4$

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[1] Wheeler : Am. J. Sci., (3), 45, 267.

Plumbic Salts.[1]

2 : 1	
$2NH_4Cl.PbCl_4$	$2RbCl.PbCl_4$
$2KCl.PbCl_4$	$2CsCl.PbCl_4$

Thorium Salts.[2]

3 : 1	2 : 1
$3CsCl.ThCl_4.12H_2O$	$2KF.ThF_4.4H_2O$ $2CsCl.ThCl_4.11H_2O$

1 : 1	1 : 2
$KF.ThF_4.\frac{1}{2}H_2O$	$KCl.2ThCl_4.18H_2O$

V. SALTS OF QUINQUIVALENT NEGATIVE METALS.[3]

4 : 1	2 : 1	1 : 1
$4NH_4Cl.SbCl_4$	$2KF.AsF_5$	$KF.AsF_5$
	$2NH_4F.SbF_5$	$NH_4F.SbF_5$
	$2KF.SbF_5$	$NaF.SbF_5$
	$2KF.NbF_5$	$KF.SbF_5$
	$2RbF.NbF_5$	
	$2NH_4F.TaF_5$	
	$2NaF.TaF_5$	
	$2KF.TaF_5$	
	$2RbF.TaF_5$	

Upon examining this table a marked similarity is to be noticed in the different series; the 2 : 1 and 1 : 1 types are common to all; the 4 : 1, 3 : 1, 3 : 2, and 1 : 2 types are found in all but one; while 2 : 3 types are found in three of the series. Besides the seven types just mentioned there are eight others, but only one of the latter exists in more than one series, and most of them are represented by only a single salt. It is quite possible that some of these unusual ratios are due to erroneous descriptions of salts, but it is certain that many of them represent real compounds.

The remarkable similarity in the prominent types of the

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[1] Am. J Sci., (3), 46, 180.

[2] The salt $8NH_4Cl.ThCl_4.8H_2O$, described by Chydenius as a sintered mass, is rejected, as is also $8KF.7ThF_4.6H_2O$, which Chydenius himself considered to be probably a mixture.

[3] Pennington's salts, $7CsF.NbF_5$ and $15CsF.TaF_5$, are omitted because they differ entirely from two rubidium salts obtained in the same investigation (which are given in the list), and because they depend upon single partial analyses (see J. Am. Chem. Soc., 18, 59). It is impossible to believe that caesium and rubidium salts of the same metals should differ so widely as these appear to do.

Types Arranged According to the Valency of the Negative Metals.

In this table the number of salts given in the preceding lists is placed under each type :

Valency.																Total
I	....	....	3 : 1 1	....	....	2 : 1 6	3 : 2 1	....	1 : 1 7	....	2 : 3 1	....	1 : 2 1	....	....	17
II	....	4 : 1 9	3 : 1 11	....	....	2 : 1 78	3 : 2 1	....	1 : 1 83	....	2 : 3 4	....	1 : 2 13	....	1 : 5 2	201
III	5 : 1 1	4 : 1 3	3 : 1 46	5 : 2 1	7 : 3 5	2 : 1 48	3 : 2 23	....	1 : 1 45	3 : 4 1	....	4 : 7 1	1 : 2 3	1 : 3 1	....	178
IV	....	4 : 1 2	3 : 1 3	5 : 2 1	....	2 : 1 66	3 : 2 1	5 : 3 1	1 : 1 8	....	2 : 3 1	....	1 : 2 1	....	....	84
V	....	4 : 1 1	....	....	....	2 : 1 9	....	....	1 : 1 4	....	....	....	....	....	....	14
Total	5 : 1 1	4 : 1 15	3 : 1 61	5 : 2 2	7 : 3 5	2 : 1 207	3 : 2 26	5 : 3 1	1 : 1 147	3 : 4 1	2 : 3 6	4 : 7 1	1 : 2 18	1 : 3 1	1 : 5 2	494

series of different valencies leads to the conclusion that *the valency of a negative halide has no influence upon the types of double salts that it forms.* For, if valency had an influence it would be expected that the five series would show marked differences from one another, and probably the halides of higher valency would tend to combine with a larger number of alkaline halide molecules. Instead of a progression of types as valency increases, however, the table shows a marked symmetry in types, and their arithmetical limits in both directions are as nearly constant as could be expected, considering the variations in the numbers of known salts in the different series. The prominence of the 3 : 1 and 3 : 2 types in the trivalent series may perhaps be taken as an indication that the rule is not absolute, but since these types are not the only prominent ones, and since both of them occur in three other series, the circumstance that many are found in the trivalent series may be accidental.

The facts, mentioned above, that the ratios of the different series are nearly symmetrical and that the arithmetical limits of the types in *both directions* are nearly uniform appear to be important, for they indicate that the ratios according to which positive and negative halides combine are not influenced to any great degree by the positive or negative nature of the halides. In other words, *the molecules of alkaline halides possess nearly the same combining power as molecules of negative halides.* Perhaps this point may be made clearer by the statement that if all the ratios in the table are read backward they remain almost unchanged in their arithmetical aspect, and in the cases of most of the prominent ratios there is actually no change; for instance, the list of ratios 5 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2, 1 : 3, and 1 : 5 is the same whether read forward or backward, and to these ratios belong almost 95 per cent of the salts here considered. It is evident, however, that positive and negative halides are not of *exactly* equal numerical importance, for to the left of the 1 : 1 ratio in the table, toward the positive halide end, the ratios are more numerous and the salts far more abundant than toward the negative halide end; it appears to be the 3 : 2 ratio column that forms a nearly symmetrical dividing line between the positive and negative ends, and even with this division the salts on the positive side predominate in number.

Another point to which attention may be called is that *salts of simple types predominate.* More than 71 per cent of the salts in the list belong to the 2 : 1 and 1 : 1 ratios, while the 4 : 1, 3 : 1, 3 : 2, 2 : 3, and 1 : 2 ratios represent over 25 per cent of them. The remaining eight types, most of which are more complex, include less than 3 per cent of all the salts. The fact that the 2 : 1 and 1 : 1 ratios are so important in *all* the series, is another indication that valency does not influence the ratios according to which halides combine. Another evidence of simplicity is the circumstance, that as far as is known, not more than 5 molecules of one halide can combine with 1 molecule of another in extreme cases, while the usual limit is 2, 3, or 4. It is undoubtedly a fact that there are a few complicated salts which are not derived from mixtures or poor analyses. For example, the antimony salts to which is here given the 7 : 3 ratio have been thoroughly investigated, and, without doubt, possess either this ratio or one still more complex.

The conclusions that have been reached above are not encouraging in the way of giving an insight to the structure of double halides, for, if valency plays no part in this, the number of halogen atoms likewise has no influence, and such laws or rules, based on halogen atoms, as have been advanced must be abandoned. Professor Remsen's law,[1] which states that the number of alkaline halide molecules that can combine with a negative halide molecule is not greater than the valency of the latter, is evidently one of these. The dotted line in the table of ratios shows a region in the upper left-hand corner which is beyond the domain of this law. At the time that the law was brought forward it seemed reasonable, for there were only two or three possible exceptions to it. With our present knowledge of the subject, however, it is evident that it is an accidental circumstance that the law applies to so many double halides, for it is the small number of known double halides of univalent negative metals, as well as the rarity of salts of high alkali-metal ratios in the subsequent series, which determines the comparatively small number of exceptions to this rule. Werner's theory,[1] depending as it does upon definite numbers of halogen and other atoms, appears to have no application to the double halides in general. Possibly it may apply to the salts that form complex ions in solution.

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[1] This JOURNAL, 11, 296; 14, 85.

A prevalent idea concerning the influence of valency in the formation of simple oxygen salts seems to need revision also, for halogen and oxygen salts appear to be governed by the same laws. For instance, there is no good reason for considering the valency of sulphur to have an influence upon the types of sulphates that can exist, and consequently for imagining an ideal or "ortho" sulphate such as K_6SO_6.

As far as double oxygen salts are concerned, there can be little doubt that they are analogous to double halogen salts. Their molecules usually unite in 2 : 1 or 1 : 1 ratios. A double oxygen salt, however, in view of the analogy between double halogen and simple oxygen salts, may be considered as analogous to a double-double halogen salt, if such there be. Possibly some of the complex types of double halogen salts may be due to such combinations; for instance, $2Rb_3SbCl$ (unknown) $+ RbSbCl_4 = 7RbCl.3SbCl_3$.

The stability of double halogen salts when they are dissolved in water varies exceedingly, but since gradations occur, and there is no sharp dividing line between classes of different stability, it cannot be supposed that there is any real difference in structure, as far as the solid state is concerned, between these different classes. In fact, salts that are isomorphous and evidently strictly analogous, vary greatly in their behavior in solution; for example, the octahedral salts K_2PtCl_6, K_2SnCl_6, and K_2PbCl_6.

Although only two classes of double salts, based on their behavior in solution, are usually recognized, there are three more or less distinctly defined groups, the first, of which K_2PtCl_6 is an example, undergoes ionization into alkali-metal ions and complex negative ions, with little or no decomposition into the simple halides. It is this class which displays a striking similarity to simple oxygen salts. They are comparatively few in number, but the double cyanides, which are probably entirely analogous to double halides, furnish many examples of them. The second group consists of salts that readily separate into their component halides in solution, but which may be recrystallized unchanged from water or from dilute acid solutions. To the third class belong salts that require the presence of an excess of one of their halides in solution in order that they may be formed. Sometimes the excess required is very great, so that the proportion of halides in the solution is widely different from that in the salt that crystallizes out. It is by varying the proportions of two halides greatly that a series of several double salts may sometimes be produced from them.

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[1] Ztschr. anorg. Chem., 3, 267.

The fact that the same two halides may unite in several proportions to form different double salts is a point that has been sometimes disregarded by chemists. Some investigators have been content with the preparation of a single compound in cases where several might have been produced. This is a matter that should be borne in mind in the study of the physical properties of solutions. The largest number of double halides that have been produced by combining two simple halides appears to be five; for instance, five caesium mercuric chlorides and five caesium antimonious fluorides are the most extensive series of this kind that are known. Such series appear to be limited by a sort of overlapping of conditions, for compounds that are expected from analogy, intermediate between two that are produced, often cannot be prepared, and where a single double salt is very stable it may be the only one that can be made. Where several double halides of the same two simple halides exist, it is usually the case that one of them is the most stable one and that this is produced by the recrystallization of the others, but cases occur where two of the salts, at least, are unchanged by recrystallizing.

The water of crystallization of double halides appears to present precisely the same problem as in the case of simple salts, for we find double salts of the same type possessing no water and varying quantities of it, and no good evidence is to be found that in these compounds a molecule of water is equivalent to an alkaline halide molecule, a relation similar to that, for example, that has been supposed to exist between the compounds $FeSO_4.7H_2O$ and $FeSO_4.(NH_4)_2SO_4.6H_2O$.

It has been pointed out previously[1] that double halides seem to show an increase in stability and variety from the iodides to the chlorides, and apparently also to the fluorides. It is probable that this is a general rule among these compounds.

It has been shown[2] also that with the metals magnesium, zinc, cadmium, and mercury the tendency to form double halides increases with the atomic weights. This tendency is found in other cases also, but from a comparison of the zirconium and thorium salts, as well as the antimonious and bismuth salts, it seems doubtful that this is a rule that applies in all cases.

It has been found in some cases[3] that caesium appears to form more extensive series of double salts than the other alkali metals, but evidently there are exceptions to this rule, for Wells and Campbell[4] were unable to prepare any caesium magnesium iodide, although both ammonium and potassium magnesium iodides are known.

The rule advanced by Godeffroy[5] that all the double salts of caesium are less soluble than those of the other alkali metals, while true in most instances, is apparently not invariable, for Wells and Campbell[6] found that the 1 : 1 caesium-zinc salts, if they exist at all, are too soluble to be crystallized in a satisfactory condition, although corresponding ammonium and potassium salts are known.

Professor Remsen[7] called attention to the fact that certain double halides show gradations in water of crystallization, increasing with the atomic weight of the halogen and decreasing with the atomic weight of the alkali metal. An inspection of the list of salts shows that there are many instances of analogous salts to which these rules apply, particularly in the larger amounts of water in sodium and lithium salts and in iodides, and the smaller amounts of water in caesium salts and in fluorides; but, taking the list as a whole, these gradations are not very striking, and there are a few apparent exceptions to them.

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[1] Am. J. Sci., (3), **46**, 432.

[2] *Ibid.*, (3), **46**, 434.

[3] *Ibid.*, (3), **46**, 223.

[4] *Ibid.*, (3), **46**, 432.

[5] Ber. d. chem. Ges., **9**, 1365.

[6] Am. J. Sci., (3), **46**, 434.

[7] This JOURNAL, **14**, 88.

It has been noticed in some cases that caesium halides combine with a greater number of negative halide molecules than do other alkaline halides, while at the other end of a series more molecules of a lighter alkaline halide than of a caesium halide may combine with a negative halide. For instance, the caesium-zirconium and potassium-zirconium fluorides[1] show this relation in the following ratios of their salts:

$CsF : ZrF_4$	....	2 : 1	1 : 1	2 : 3
$KF : ZrF_4$	3 : 1	2 : 1	1 : 1	....

This is evidently not a general rule, however, for there is a 1 : 5 ammonium mercuric chloride corresponding to the extreme type of caesium mercuric chlorides, while at the positive end the caesium lead and caesium-mercuric salts extend farther than the salts of other alkali metals.

Many irregularities appear in the list. Sometimes fluorides, chlorides, bromides, and iodides seem to be analogous, but often they are not. There are some curious relations of this sort. For instance, all the double fluorides of tellurium are 1 : 1 salts while the other tellurium salts belong to the 2 : 1 type; there is only one chloride among twelve 1 : 1 thallic salts, while all the 2 : 1 salts and nearly all the 3 : 1 salts are chlorides.

Perhaps the most marked case of uniformity in double halides is the invariability of the 2 : 1 type in the salts of the quadrivalent platinum group metals, and this type predominates to a remarkable extent among the salts of the other quadrivalent elements. There are several other well marked groups, such as the 1 : 1 magnesium salts with 6 molecules of water, the 2 : 1 chromium and ferric salts with one water, and the 3 : 2 anhydrous arsenious, antimonious, and bismuth salts.

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[1] Wells and Foote: Am. J. Sci., (4), 1, 18.

It may be stated that in our study of double halides about one-third of the compounds given in the list have been prepared in this laboratory. Some indications of regularity have been observed in connection with these researches, but it must be admitted that the results have been negative as far as throwing light upon the structure of this class of compounds is concerned.

Summary.

In the present discussion, by the method of comparison, the most important conclusion appears to be that the valency of negative halides has little or no influence upon the types of double halides that they form.

It has been shown also that the combining power of negative halides, whatever their valency may be, is nearly the same as that of alkaline halides.

Attention has been called to the prominence of simple types among these double salts.

It has been pointed out that double halides probably increase in ease of formation and variety from the iodides to the fluorides ; but that other gradations and analogies which exist in some cases are probably not general.

The classification of double halides into three groups based upon their behavior in solution has been advocated. (1) Salts that form complex ions. (2) Other salts that can be recrystallized from water or dilute acids. (3) Salts that require the presence of an excess of one of their components for their formation.

NEW HAVEN, CONN., May, 1901.

LXXXVIII.—ON SOME ACETYL AND BENZOYL-PSEUDOTHIOUREAS.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

In a previous paper it was shown that the acylimidomonothiocarbonic esters,

$$RCON{=}C(OCH_3)SCH_3,$$

react with amines[1] as readily as with ammonia.[2] In these reactions the mercapto group is removed and acylpseudoureas are formed,

$$RCON{=}C(OCH_3)NHR.$$

The fact was also established that the phenylimidomonothiocarbonic esters, $C_6H_5N = C(OCH_3)SCH_3$, and the hydrazone of thiocarbonic ethyl ester,

$$C_6H_5NH{-}N{=}C(OC_2H_5)SC_2H_5,$$

do not react in an analogous manner. Indeed these imido esters show a noteworthy inertness when treated with organic bases.[3]

Experiments with the acylimidodithiocarbonic esters,[4]

$$RCON{=}C(SCH_3)_2,$$

have now shown that these compounds give acylpseudothioureas. The action takes place in the cold, and more smoothly than in the case of the corresponding monothioesters,

$$C_6H_5CON{=}C(SCH_3)_2 + HNRR' = C_6H_5CON{=}C(SCH_3)NRR' + HSCH_3.$$

This adds another series to the known types of acyclic pseudothioureas. The simple derivatives of the structure

$$HN{=}C(SR)NH_2.HX$$

were investigated by Claus,[5] Bernthsen and Klinger;[6] the mononitrogen-substituted compounds by Werner[7] and Bertram;[8] while the disubstituted derivaties have been studied by Will, Rathke, Bielschowsky, Reimarus, Evers, Förster, and Noah.[9]

The nearest analogue to our compounds is the monacetylthiolethylisodiphenylthiourea,

$$C_6H_5N{=}C(SC_2H_5)N(C_6H_5)COCH_3,$$

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[1] This JOURNAL, **24**, 189 (1900).

[2] Dixon: J. Chem. Soc. (London), **75**, 378 (1899).

[3] This JOURNAL, **24**, 60, 423 (1900).

[4] *Ibid.*, **26**, 185 (1901).

[5] Ber. d. chem. Ges., **7**, 236 (1874); *Ibid.*, **8**, 41; Ann. Chem. (Liebig), **179**, 145 (1875).

[6] Ber. d. chem. Ges., **11**, 492 (1878); **12**, 575.

[7] J. Chem. Soc. (London), **57**, 283 (1890).

[8] Ber. d. chem. Ges., **25**, 48 (1892).

[9] *Ibid.*, **14**, 1485, 1774 (1881); **15**, 338, 1309 (1882); **19**, 2348 (1886); **21**, 967, 1857 (1888); **23**, 2195 (1890).

of Dains,[1] and this is the only acylpseudothiourea which has hitherto been obtained. This was prepared by the action of acetyl chloride on ethyldiphenylpseudothiourea ; but while it is described as an uncrystallizable oil, most of our compounds, on the other hand, are remarkable for their great tendency to crystallize and for the ease with which they can be purified.

Since the acylpseudothioureas have the structure of amides, amidines, and thioimidoesters combined, it seemed that some of the various cases of structural and stereochemical isomerism, theoretically possible for these compounds, might be met with in this new series. We have therefore prepared benzoylthiolbenzylphenylpseudothiourea,

$$C_6H_5CON{=}C(SCH_2C_6H_5)NHC_6H_5,$$

by the following four methods :

I. The action of aniline on benzoylimidodithiobenzyl carbonate.

II. The action of benzoic anhydride on phenylpseudobenzylthiourea.

III. The action of benzyl chloride on an aqueous sodium-hydrate solution of benzoylphenylthiourea.

IV. The action of benzyl chloride, benzoylphenylthiourea and alcoholic sodium ethylate.

Each of these methods gave one and the same compound, and no evidence was observed of the formation of isomeric products.

The acylpseudothioureas appear to have no basic properties. They do not combine with picric acid. Those which contain a —NH— group are soluble in alkali. Those derived from secondary amines can be distilled at reduced pressure unaltered, while those prepared from primary amines decompose on heating with the formation of mercaptan, substituted acid amides, and other products. A smooth decomposition into carbodiimide derivatives was not observed.

When treated with hydrochloric acid they do not give normal acylureas, as in the case of the oxygen analogues, but decompose or undergo hydrolysis as follows :

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[1] J. Am. Chem. Soc., **22**, 197 (1900).

$$C_6H_5CON{=}C(SC_2H_5)NHC_6H_5 + H_2O + HCl = C_6H_5CONHCO.SC_2H_5 + C_6H_5NH_2HCl.$$

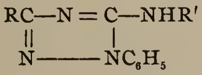
When treated with alcoholic ammonia guanidine derivatives are formed :

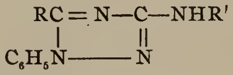
$$C_6H_5CON{=}C(SC_2H_5)NHC_6H_5 \longrightarrow C_6H_5CON{=}C(NH_2)NHC_6H_5.$$

This affords new proof that both of the alkyl groups in the acylimidodithiocarbonic esters are attached to sulphur.

Guanidine derivatives were not obtained by the action of aniline. When the esters were heated with this base they underwent decomposition and benzanilide was obtained.

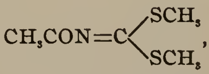
The acylpseudothioureas readily react with phenylhydrazine to form aminotriazoles. Which of the two following formulas represents the structure of these products will be decided later :





EXPERIMENTAL PART.

Dimethyl Acetylimidodithiocarbonate,[1]



$$CH_3CON{=}C\begin{cases}SCH_3\\SCH_3\end{cases},$$

and Alcoholic Ammonia.—Five grams of the ester were allowed to stand for several days with an excess of the ammonia solution. On evaporating the alcohol, an oil was obtained which showed no signs of solidifying on standing. That this consisted mostly of guanidine was shown by mixing with an alcoholic solution of picric acid, whereupon an immediate precipitate of guanidine picrate[2] resulted. Nitrogen determinations gave :

	Calculated for $C_7H_8O_7N_6$.	Found. I.	II.
N	29.16	29.14	29.04

Acetyldiisobutylthiolmethylpseudothiourea, $CH_3CON{=}C(SCH_3)N(C_4H_9)_2$.—Dimethyl acetylimidodithiocarbonate and diisobutylamine reacted at ordinary temperatures. The product was a yellow oil which distilled under 22 mm. pressure at 175° to 177°. A middle portion of this gave, on analysis, the following result :

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[1] Wheeler and Johnson : This JOURNAL, *Loc. cit.*

[2] Emich : Monatsh. Chem., **12**, 23 (1891).

	Calculated for $C_{12}H_{24}ON_2S$.	Found.
N	11.47	11.80

Acetylphenylthiolmethylpseudothiourea, $CH_3CON{=}C(SCH_3)NHC_6H_5$. — When aniline was mixed with dimethylacetylimidodithiocarbonate, mercaptan was evolved in the cold, and, after twelve hours, the material completely solidified. This pseudothiourea crystallized from dilute alcohol in beautiful, long, colorless needles, and melted at 82° to 83°. A nitrogen determination gave :

	Calculated for $C_{10}H_{12}ON_2S$.	Found.
N	13.46	13.31

Benzoylparatolylthiolmethylpseudothiourea, $C_6H_5CO.N{=}C(SCH_3)NHC_6H_4CH_3$.—Dimethyl benzoylimidodithiocarbonate and *p*-toluidine were warmed on the steam-bath until mercaptan ceased to be evolved. On cooling, a solid mass was obtained which crystallized from alcohol in beautiful prisms and melted at 130°. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}ON_2S$.	Found.
N	9.85	9.83

Benzoyl-α-naphthylthiolmethylpseudothiourea, $C_6H_5CON{=}C(SCH_3)NHC_{10}H_7$. —Dimethyl benzoylimidodithiocarbonate and α-naphthylamine gave a product which crystallized from alcohol in balls of fine needles. These melted at 124° and a nitrogen determination gave :

	Calculated for $C_{19}H_{16}ON_2S$.	Found.
N	8.75	8.44

Benzoylmetanitrophenylthiolmethylpseudothiourea, $C_6H_5CON{=}C(SCH_3)NHC_6H_4NO_2$.—Dimethyl benzoylimidodithiocarbonate and metanitraniline readily reacted on warming. The product was soluble in hot alcohol and crystallized in needle-like prisms which melted at 71° to 72°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}O_3N_3S$.	Found.
N	13.44	13.33

Acetyldiethylthiolethylpseudothiourea, $CH_3CON{=}C(SC_2H_5)N(C_2H_5)_2$. — Diethyl acetylimidodithiocarbonate and diethylamine gave a yellow oil which distilled at 162° to 164° at 21 mm. pressure. A nitrogen determination in a middle portion of this gave :

	Calculated for $C_9H_{18}ON_2S$.	Found.
N	13.86	13.72

Acetylmethylphenylthiolethylpseudothiourea, $CH_3CON{=}C(SC_2H_5)N(CH_3)C_6H_5$, from the ethyl dithiocarbonate and methyl aniline, crystallized beautifully, from petroleum ether, in colorless prisms and melted at 66°. A nitrogen determination gave :

	Calculated for $C_{12}H_{16}ON_2S$.	Found.
N	11.86	11.87

Benzoyldiethylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_2H_5)_2$, formed colorless rectangular prisms, which melted at 70°, when crystallized from petroleum ether. A nitrogen determination gave :

	Calculated for $C_{14}H_{20}ON_2S$.	Found.
N	10.60	10.61

Benzoyldipropylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_3H_7)_2$, was obtained as a yellow oil, boiling for the most part at 226° to 229° at 17 mm. pressure. A nitrogen determination in a middle sample of this gave :

	Calculated for $C_{16}H_{29}ON_2S$.	Found.
N	9.59	9.84

Benzoyldiisobutylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_4H_9)_2$, formed an oil which boiled at 234° to 236° at 21 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{18}H_{28}ON_2S$.	Found.
N	8.75	8.65

Benzoylparatolylthiolethylpseudothiourea, $C_6H_6CON{=}C(SC_2H_5)NHC_6H_4CH_3$.—This crystallized from alcohol in needle-like prisms, which melted at 93°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
N	9.40	9.24

When this pseudothiourea was heated on the steam-bath with phenylhydrazine, until mercaptan ceased to be evolved, a solid product was obtained which crystallized from alcohol in stout prisms and melted at 225° to 226°. A nitrogen determination gave results agreeing with those calculated for diphenylparatolylaminotriazole :

	Calculated for $C_{21}H_{18}N_4$.	Found.
N	17.14	17.01

Benzoylpseudocumylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)NHC_6H_2(CH_3)_3$, crystallized from alcohol in a mass of fine needles. These melted at 83° to 84°, and a nitrogen determination gave :

	Calculated for $C_{19}H_{22}ON_2S$.	Found.
N	8.60	8.84

Benzoylparaanisylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)NHC_6H_4OCH_3$, crystallized from alcohol in fine, needle-like prisms, which melted at 99° to 100°. The nitrogen determination was as follows :

	Calculated for $C_{17}H_{18}O_2N_2S$.	Found.
N	8.91	8.83

Benzoyldiphenylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_6H_5)_2$, crystallized from a mixture of benzene and petroleum ether in colorless prisms, and melted at 142°. A nitrogen determination gave :

	Calculated for $C_{22}H_{20}ON_2S$.	Found.
N	7.77	7.80

Benzoylphenylthiolpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_5$, from propyl dithiocarbonate and aniline formed beautiful colorless prisms, from alcohol, melting at 78° to 79°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
N	9.39	9.51

Benzoylparatolylthiolpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_4CH_3$, crystallized from alcohol in colorless needles and melted at 81° to 81°.5. A nitrogen determination gave :

	Calculated for $C_{18}H_{20}ON_2S$.	Found.
N	8.97	9.13

Benzoylmetachlorphenylthiolnormalpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_4Cl$, formed colorless prisms, from alcohol, which melted at 59° to 59°.5, and a nitrogen determination gave :

	Calculated for $C_{17}H_{17}ON_2ClS$.	Found.
N	8.42	8.59

Benzoylphenyleneguanidine, $C_6H_5CO.N{=}C(NH)_2C_6H_4$. — Diethyl benzoylimidodithiocarbonate, orthophenylenediamine hydrochloride, and sodium ethylate were warmed on the steam-bath. On cooling and crystallizing the product from alcohol, minute, colorless prisms separated, which melted at 237°. This material was insoluble in chloroform, benzene, and water. It was free from sulphur, and a nitrogen determination gave :

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.63

Diphenylene-di(benzoylthiolethylpseudothiourea), $C_6H_5CON{=}C(SC_2H_5)NHC_6H_4.C_6H_4NH(C_2H_5S)C{=}NCOC_6H_5$.—This compound was obtained when diethyl benzoylimidodithiocarbonate was mixed with benzidine in the proportion of either 1 or 2 molecules of the ester to 1 of the amine. It was difficultly soluble in alcohol, chloroform, and benzene; from a mixture of benzene and alcohol colorless needles were obtained which melted at 179° with slight effervescence. A nitrogen determination gave:

	Calculated for $C_{32}H_{30}O_2N_4S_2$.	Found.
N	9.87	9.80

When this dipseudothiourea was warmed on the water-bath with phenylhydrazine, mercaptan was evolved and a residue difficultly soluble in alcohol was obtained. It formed poorly defined crystals from alcohol which did not melt below 265° and a nitrogen determination agreed with the percentage calculated for a ditriazole of the formula

$$(C_6H_5)_2C_2N_3NHC_6H_4.C_6H_4NHC_2N_3(C_6H_5)_2:$$

	Calculated for $C_{40}H_{30}N_8$.	Found.
N	18.00	17.80

Dimethoxydiphenylene-di-(benzoylthiolethylpseudothiourea), $C_6H_5CON{=}(CSC_2H_5NHC_6H_3OCH_3.C_6H_3OCH_3NH(C_2H_5S)C{=}NCOC_6H_5$.—Diethyl benzoylimidodithiocarbonate and *o*-dianisidine formed a difficultly soluble compound which crystallized from a mixture of benzene and alcohol in minute, colorless needles. It melted at 170° to 171°, and a nitrogen determination gave:

	Calculated for $C_{34}H_{34}O_4N_4S_2$.	Found.
N	9.12	9.06

Benzoylphenylthiolbenzylpseudothiourea, $C_6H_5CON{=}C(SCH_2C_6H_5)NHC_6H_5$. — This compound was prepared by the four methods mentioned in the introduction. It crystallized from alcohol in small, colorless prisms, which melted at 116° to 117°, and a nitrogen determination gave:

	Calculated for $C_{21}H_{18}ON_2S$.	Found.
N	8.09	8.09

When this pseudothiourea was warmed with aqueous hydrochloric acid, a compound crystallizing from alcohol in colorless, needle-like prisms, and melting at 141° to 142°, was obtained. A nitrogen determination agreed with the composition calculated for benzoylthiobenzylcarbamate,

$$C_6H_5CONHCO.SCH_2C_6H_5 :$$

	Calculated for $C_{15}H_{13}O_2NS$.	Found.
N	5.16	5.16

On dissolving the pseudothiourea (5 grams) in alcoholic ammonia and allowing the solution to stand for nine days and then evaporating, an oil was obtained. When this was treated with alcohol a mass of crystals separated, melting at 70° to 71° (benzyl disulphide). To the alcoholic solution picric acid was added; a precipitate was formed at once, and on crystallizing from alcohol bright-yellow prisms, melting at 186°, were obtained. A nitrogen determination agreed with the composition calculated for benzoylphenylguanidine picrate, $C_6H_5CON{=}C(NH_2)NHC_6H_5.C_6H_2(NO_2)_3OH$:

	Calculated for $C_{20}H_{16}O_8N_6$.	Found.
N	17.94	17.67

This compound was also obtained by the action of alcoholic ammonia on benzoylphenylthiolethylpseudothiourea and then treating the product with picric acid.

Benzoylphenylguanidine, $C_6H_5CON{=}C(NH_2)NHC_6H_5$, was obtained by treating the picrate with an aqueous solution of sodium hydrate. It was soluble in alcohol and benzene, and it crystallized from a mixture of benzene and petroleum ether in minute, light-yellow prisms, which melted at 90° to 91°. A nitrogen determination gave :

	Calculated for $C_{14}H_{13}ON_3$.	Found.
N	17.57	17.55

Benzoylphenylthiolmetaxylylpseudothiourea, $C_6H_5CON{=}C(SCH_2C_6H_4CH_3)NHC_6H_5$, from dimetaxylyl benzoylimidodithiocarbonate and aniline, crystallized in colorless prisms and melted at 110° to 111°. A nitrogen determination gave :

	Calculated for $C_{22}H_{20}ON_2S$.	Found.
N	7.77	7.82

Benzoyl-α-naphthylthiolmetaxylylpseudothiourea, $C_6H_5CON{=}C(SCH_2C_6H_4CH_3)NHC_{10}H_7$, formed colorless, flattened prisms from alcohol, melting at 133°. A nitrogen determination gave :

	Calculated for $C_{26}H_{22}ON_2S$.	Found.
N	6.83	6.84

New Haven, Conn., May 30, 1901.

LXXXIX.—ON THE MIXED CRYSTALS OF COPPER SULPHATE AND ZINC SULPHATE.

By H. W. Foote.

Two salts of distinct chemical composition may separate from a solution containing a mixture of the two, in homogeneous crystals, containing both of the salts in indefinite proportions. These are known as "mixed crystals." They may be roughly divided into two classes, the first including those in which the salts may mix in all proportions, and the second including those in which one salt is capable of mixing with but a limited amount of the other.

The alums are an example of the first class. Thus, ammonium and potassium alums can form mixed crystals which contain any desired quantity of either constituent.

The mixed crystals of beryllium sulphate and beryllium selenate are an example of the second class. At ordinary temperatures, tetragonal $BeSO_4.4H_2O$ forms mixed crystals with $BeSeO_4.4H_2O$, ranging from pure $BeSO_4.4H_2O$ to the molecular proportion 7.33 $BeSO_4.4H_2O$: $BeSeO_4.4H_2O$; but no larger proportion of $BeSeO_4.4H_2O$ can exist with $BeSO_4.4H_2O$ in stable tetragonal crystals. If more of the former is introduced, the crystal form changes to orthorhombic, and a series of mixed crystals in this form may be prepared, in which the molecular proportion ranges from $4BeSO_4.4H_2O$: $BeSeO_4.4H_2O$ to pure $BeSeO_4.4H_2O$.[1]

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[1] Van 't Hoff : "Vorlesungen über Chemie," Vol. I, p. 49.

If mixed crystals are considered as solid solutions, the salts of the first class, which crystallize together in all proportions, may be compared to perfectly miscible liquids like alcohol and water, while salts of the second class, whose isomorphism is limited, resemble partially miscible liquids, like aniline and water.

As van 't Hoff has pointed out, the composition of the mixed crystals of salts which belong to the second class—*i. e.*, which are only partially miscible with each other—and which are formed at the mixing limit,[1] ought to be a function of the temperature.

There may also be cases in which two salts will combine in all proportions to form mixed crystals within a certain range of temperature, like those of the first class named above, while outside of this range each salt can mix with but a limited amount of the other, like those of the second class; just as aniline mixes in all proportions with water at temperatures above 165°, while below that limit it only mixes to a limited extent.

Roozeboom[2] also states that the composition of mixed crystals should change with the temperature.

These theoretical conclusions are supported by a consideration of the phase rule of Gibbs; for it is clear that any mixed salt has reached its stable mixing limit when there are deposited from its solution crystals of another form. Thus, tetragonal $BeSO_4.4H_2O$ will contain a maximum of $BeSeO_4.4H_2O$ when the concentration of the solution from which it crystallizes is such that the solution is also saturated in regard to the orthorhombic mixed crystals of $BeSeO_4.4H_2O$ containing $BeSO_4.4H_2O$; in other words, when the two forms crystallize together. In such a system there are four phases—vapor, solution and the two solid phases; and three components—the two salts and water. It therefore follows that if we change one of the possible variable conditions, the others will be fixed. This may be seen if the phase rule be expressed in the form: $V = C + 2 - P$, where V represents the number of physical conditions which may be varied, C the number of components present, and P the number of phases. Hence, $V = 3 + 2 - 4 = 1$. The variable conditions are temperature, pressure, and the concentration of the solution and each solid phase. If the temperature be changed, it follows that the other variables must change. With fixed temperature, the concentration of each phase and the vapor pressure must be fixed.

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[1] The term "mixing limit" ("Mischungs-grenze") is used in this paper to represent the composition of mixed crystals of one salt with a maximum of another. Thus, tetragonal mixed crystals of beryllium sulphate and beryllium selenate have reached the mixing limit when their composition is 7.33 $BeSO_4.4H_2O : BeSeO_4.4H_2O$.

[2] Ztschr. phys. Chem. 8, 530.

So far as the writer knows, no systematic experiments have as yet been made to test this proposition directly, which may be stated thus: When two salts crystallize from aqueous solution, depositing mixed crystals of two crystalline forms, the composition of the crystals, at the "mixing limit," will change with the change of temperature.

The object of the present investigation was to test the influence of temperature on the "mixing limit" of copper sulphate and zinc sulphate and, as will appear below, the experiments have proved that, in accord with the theoretical conclusions adduced, the composition of the mixed crystals, at the mixing limit, changes with change of temperature.

It is well known[1] that copper sulphate, when crystallizing from solutions containing zinc sulphate, forms triclinic crystals of $CuSO_4.5H_2O$, containing a few per cent of $ZnSO_4.5H_2O$, as an isomorphous mixture. As the quantity of zinc sulphate is increased in the solution, monoclinic crystals containing $CuSO_4.7H_2O$ and $ZnSO_4.7H_2O$ in isomorphous mixture are formed, and these give place, in the presence of still more zinc sulphate, to orthorhombic crystals of $ZnSO_4.7H_2O$, containing a small amount of $CuSO_4.7H_2O$.

The following method was adopted for the present work:

Solutions of copper sulphate and zinc sulphate, mixed together and very slightly acidified with sulphuric acid, were prepared in such concentrations that they were very slightly supersaturated at the temperature of experiment.

Several hundred cubic centimeters of the mixed solutions were used in each experiment, so that the deposit of a few grams of crystals would not greatly alter the proportions of copper and zinc remaining in solution.

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[1] Retger: Ztschr. phys. Chem., **15**, 573; Stortenbeker: *Ibid.*, **22**, 60.

The solutions were seeded with a mixture of the two kinds of crystals which it was desired to have form together. Thus, if the solution was of such concentration that the orthorhombic and monoclinic heptahydrates were expected, these two forms were added in minute quantities. If the solution contained more copper sulphate, monoclinic and triclinic crystals, mixed and powdered, were introduced. In case the right proportions of copper and zinc sulphates were not present, only one form would crystallize—that which was stable under the conditions. The gradual addition of more copper or zinc solution would finally produce the conditions where both forms would crystallize together. If the crystals thus obtained were large enough to be separated mechanically, which was often the case, this was done and the separated products were analyzed. If it was impracticable to separate the two forms, they were redissolved and the solution was seeded with but one kind of crystal. The product thus obtained was usually pure, or nearly so, and could be separated mechanically from admixture and analyzed. The composition of the crystals appeared to be practically the same whichever method of separating them was adopted.

The experiments were carried out at five different temperatures, 12°, 25°, 35°, 40°, and 45° C. For maintaining a constant temperature of 12° a thermostat was used, which I have previously described.[1] As the work was done in the winter of 1900–1901, when the temperature of the city water supply ranged between 4° and 8° C., it was unnecessary to cool the water with ice before passing it into the thermostat. An Ostwald thermostat was used to maintain a constant temperature in all other cases.

The analytical methods employed were as follows:

Copper was determined by titration with a solution of sodium thiosulphate, standardized from time to time with weighed quantities of pure copper sulphate. The details of the titration are as follows:

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[1] Ztschr. phys. Chem., **33**, 749.

The substance to be analyzed, dissolved in water, is mixed with several grams of potassium iodide dissolved in a little water. The iodine thus set free is titrated with a standard solution of sodium thiosulphate in the presence of starch paste until the blue color just disappears. The method gave entire satisfaction.

Water was determined, whenever the crystal form was uncertain, by the loss on heating very gently in a porcelain crucible till the weight was constant.

If desired, copper was determined in the residue from the water determination by dissolving in water and titrating as above described.

Zinc sulphate was always determined by difference.

The solutions from which the mixed crystals deposited were analyzed by evaporating accurately weighed quantities of them to dryness in porcelain crucibles and igniting gently to constant weight. Copper sulphate was then determined by titration, as above described, in the aqueous solution of the ignited residue and the quantity of zinc sulphate was determined by difference.

It will be noticed below that the composition of different crops of crystals obtained under apparently the same conditions varies considerably. The same result has been noticed before,[1] but the variations in successive crops, as well as from different solutions of about the same concentration, are not great enough to affect the general results.

In tabulating the results below, the percentage of the copper sulphate hydrate is given. This is almost identical with the corresponding molecular percentage, as the atomic weights of copper and zinc are nearly the same.

At 40°, the orthorhombic heptahydrate gave place to the hexahydrate, $(CuZn)SO_4.6H_2O$, and at 45° the monoclinic heptahydrate could no longer be obtained. At this temperature the pentahydrate and the hexahydrate were obtained together.

The following results were obtained for the composition of the mixed crystals :

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[1] Mohr : Ztschr. phys. Chem., 27, 204; Stortenbeker : *Ibid.*, 34, 108.

Table I.—Percentage of Copper Sulphate Hydrate in Mixed Crystals Obtained at Different Temperatures.

Triclinic $(CuZn)SO_4.5H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.5H_2O$.	Monoclinic $(CuZn)SO_4.7H_2O$ crystallizing with pentahydrate. Percentage $CuSO_4.7H_2O$.	Monoclinic $(CuZn)SO_4.7H_2O$ crystallizing with orthorhombic heptahydrate. Percentage $CuSO_4.7H_2O$.	Orthorhombic $(CuZn)SO_4.7H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.7H_2O$.
T = 12° C.			
87.15	38.71	15.87	3.76
89.49	38.49	16.65	2.76
88.98	38.69	19.74	3.11
86.73			2.73
89.20			
T = 25° C.			
78.00	27.79	14.51	2.53
76.00	29.33	12.34	2.48
81.15	29.65	13.68	2.58
81.70	27.09		
79.38	28.41		
T = 35° C.			
68.85	25.33	10.49	1.98
68.62	25.85	11.34	2.68
67.53	25.81	13.39	2.12
	25.35	13.33	1.92
	24.63	12.85	2.33
T = 40° C.			
		Monoclinic heptahydrate crystallizing with $(CuZn)SO_4.6H_2O$ Percentage $CuSO_4.7H_2O$.	$(CuZn)SO_4.6H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.6H_2O$.
58.66	26.47	14.74	3.92
58.77	23.32	14.70	3.93
	23.76	15.33	3.68
	24.71	14.22	
		15.09	

T = 45° C.

Triclinic $(CuZn)SO_4.5H_2O$ crystallizing with hexahydrate. Percentage $CuSO_4.5H_2O$.	Hexahydrate $(CuZn)SO_4.6H_2O$ crystallizing with pentahydrate. Percentage $CuSO_4.6H_2O$.
52.12	5.99
50.51	4.46
47.04	5.90
45.08	
50.43	

From the analytical results just given the following averages are computed :

Table II.—Average Percentage of Copper Sulphate Hydrate in Mixed Crystals Obtained at Different Temperatures.

T.	Triclinic crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.5H_2O$.	Mouoclinic heptahydrate crystallizing with penta-hydrate. Percentage $CuSO_4.7H_2O$.	Monoclinic heptahydrate crystallizing with orthorhomic heptahydrate. Percentage $CuSO_4.7H_2O$.	Orthorhombic heptahydrate crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.7H_2O$.
12°	88.31	38.63	17.42	3.09
25°	79.25	28.45	13.51	2.53
35°	68.67	25.39	12.28	2.21
			Crystallizing with $(CuZu)SO_4.6H_2O$.	$(CuZn)SO_4.6H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.6H_2O$.
40°	58.72	24.56	14.82	3.84
	Crystallizing with $(CuZn)SO_4.6H_2O$.			Crystallizing with pentahydrate.
45°	49.04			5.45

The composition of the crystals at the mixing limit for different temperatures is also seen in Fig. I., the temperature being plotted as ordinate and the percentage of copper sulphate hydrate as abscissa.

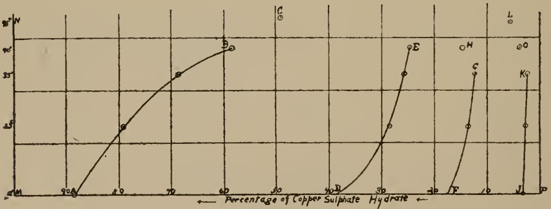

Fig. I.

The line *AB* shows the percentages of copper sulphate hydrate in the mixed pentahydrate salt which forms at the same time with monoclinic heptahydrate.

DE shows the percentages of copper sulphate hydrate in the mixed monoclinic heptahydrate salt which forms at the same time with pentahydrate.

FG shows the percentages of copper sulphate hydrate in the mixed monoclinic heptahydrate salt which forms at the same time with orthorhombic heptahydrate.

JK shows the percentages of copper sulphate hydrate in the mixed orthorhombic heptahydrate salt which forms at the same time with monoclinic heptahydrate.

As is well known, at 39° orthorhombic $ZnSO_4.7H_2O$ passes into $ZnSO_4.6H_2O$, and at 40° mixed crystals of the former could no longer be obtained, the monoclinic heptahydrate forming with the hexahydrate. The points *H* and *O* in the diagram represent the composition of these two forms at 40°. Between 40° and 45° the monoclinic heptahydrate disappears, and at 45° the pentahydrate forms with the hexahydrate. The points *C* and *L* represent the composition of the two forms at 45°. It is evident that a considerable variation in composition has but a slight effect, if any, on the transition temperature of the monoclinic heptahydrate, for while at 40° crystals of this hydrate may be obtained, varying from 24.56 per cent to 14.82 per cent of $CuSO_4.7H_2O$, at 45° it does not form at all.

In the diagram, any point in the area *JKP* represents the percentage of copper sulphate hydrate in stable mixed crystals of the orthorhombic heptahydrate.

Area *DEHGF* represents the percentage of copper sulphate hydrate in the stable mixed crystals of the monoclinic heptahydrate.

Area *NCAM* represents the percentage of copper sulphate hydrate in the stable mixed crystals of the pentahydrate.

It is evident from the results given above and from the diagram that the *composition of the mixed crystals at the mixing limit varies with the temperature.* The variation is, however, not always very great.

It was found impracticable to obtain the mixing limits of the pentahydrate and of the hexahydrate above 45°. The former could only be obtained as a very fine precipitate, and the solutions, which were necessarily very concentrated, dried very rapidly on the crystals when the latter were removed from solution. At both 50° and 55°, however, undoubted crystals of both hydrates were obtained. At 56° $CuSO_4.5H_2O$

passes into a lower hydrate.[1] *It would thus appear impossible that a complete series of stable mixed crystals of* $(CuZn)SO_4.5H_2O$ *can be prepared.*

The composition of the solutions yielding two forms of crystals was found to be as in Table III.

The values given are in molecules of copper sulphate and zinc sulphate to 100 molecules of water are plotted in Fig. II, the temperature as ordinate and the quantity of salt as abscissa.

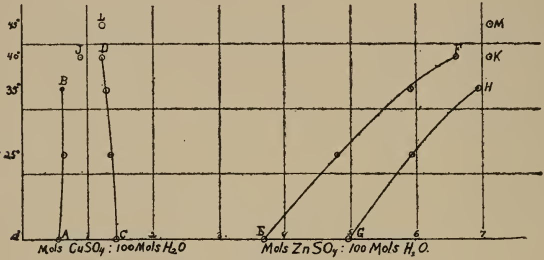

Fig. II.

Curve *AB* = mols. $CuSO_4$: 100 mols. H_2O yielding monoclinic and orthorhombic.

Curve *GH* = mols. $ZnSO_4$: 100 mols. H_2O yielding monoclinic and orthorhombic.

Curve *CD* = mols. $CuSO_4$: 100 mols. H_2O yielding monoclinic and triclinic.

Curve *EF* = mols. $ZnSO_4$: 100 mols. H_2O yielding monoclinic and triclinic.

The points *J* and *K* represent the molecules of $CuSO_4$ and $ZnSO_4$, respectively, to 100 molecules of water, in the solution yielding monoclinic salt and $(CuZn)SO_4.6H_2O$ at 40°. The points *L* and *M*, finally, represent the corresponding values at 45° for the solution yielding triclinic pentahydrate and $(CuZn)SO_4.6H_2O$. As would be expected, these points do not come into the four curves plotted.

It will be noticed in regard to the curves that the amount

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[1] Cohen: Ztschr. phys. Chem., 31, 174.

Table III.—Composition of the Solutions Yielding Two Forms of Crystals.

	Solution yielding triclinic and monoclinic crystals.					Solution yielding monoclinic and orthorhombic crystals.				
	Percentage composition.			Average number of molecules of anhydrous salt to 100 molecules of water.		Percentage composition.			Average number of molecules of anhydrous salt to 100 molecules of water.	
	$CuSO_4$.	$ZnSO_4$.	H_2O.	$CuSO_4$.	$ZnSO_4$.	$CuSO_4$.	$ZnSO_4$.	H_2O.	$CuSO_4$.	$ZnSO_4$.
12°	9.09	22.36	68.55	1.424	3.695	3.50	30.02	66.48	0.570	4.997
	8.23	23.10	68.67			3.24	29.78	66.98		
25°	7.27	28.13	64.60	1.339	4.796	3.33	33.66	63.01	0.641	5.927
	8.03	26.80	65.17			3.84	33.26	62.90		
	7.68	28.38	63.94							
35°	6.26	32.53	61.21	1.297	5.903	3.33	37.04	59.63	0.613	6.947
	7.07	32.19	60.74			3.15	37.24	59.61		
	7.65	31.85	60.50							
						Solution yielding monoclinic and $(CuZn)SO_4.6H_2O$.				
40°	6.46	34.70	58.84	1.237	6.614	4.56	37.36	58.08	0.887	7.113
	6.42	34.97	58.61			4.60	36.96	58.44		
	Solution yielding triclinic and $(CuZn)SO_4.6H_2O$.									
45°	6.38	36.25	57.37	1.227	7.105					
	6.38	36.04	57.58							
	6.25	36.68	57.07							
	5.91	36.99	57.10							

of copper sulphate in both cases remains nearly constant with rising temperature, while the quantity of zinc sulphate increases rapidly and in nearly the same ratio in the two different solutions. The change in the composition of the crystals is not so regular.

Summary.

1. Van 't Hoff has pointed out that the composition of mixed crystals at their mixing limit should be a function of the temperature.

2. The same conclusion is reached from a consideration of the application of the phase rule of Gibbs to the matter.

3. The experiments above described demonstrate that this theoretical conclusion reached by van 't Hoff and by the application of the phase rule is correct for mixtures of copper and zinc sulphates, *i. e.*, the composition of stable mixed crystals of copper sulphate and zinc sulphate formed at the mixing limit depends upon and varies with the temperature.

4. That while the composition of the mixed crystals varies with the temperature, the salts named do not form completely isomorphous crystals between 12° and 56° C.

5. That in solutions yielding two forms of crystals, the amount of copper sulphate in solution remains nearly constant with rising temperature, while the amount of zinc sulphate increases very largely with rising temperature.

NEW HAVEN, CONN., June 21, 1901.

THE DISSOCIATION OF CERTAIN ACIDS, BASES, AND SALTS AT DIFFERENT TEMPERATURES.[1]

BY HARRY C. JONES AND JAMES M. DOUGLAS.

Historical Review.

Arrhenius[2] has pointed out the connection between the depression of the freezing-point of a solvent by an electrolyte, and the conductivity of the electrolyte. In most of the earlier experiments, however, the values obtained for the amount of dissociation at zero by the freezing-point method were generally a little lower than those obtained by the conductivity method at 18° or 25°. This would indicate that there is a small temperature coefficient of dissociation.

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[1] From the dissertation of J. M. Douglas, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1901.

[2] Ztschr. phys. Chem., 1, 631.

The first piece of work to determine the electrical conductivity at zero was carried out by Wood.[1] He found that the dissociation for very dilute solutions at 0° and 18° is the same. The electrolytes used by him were potassium chloride, sodium chloride, dichloracetic acid, and trichloracetic acid. He did not carry his work far enough to obtain μ_∞, but calculated this by means of temperature coefficients, from the work of Kohlrausch and Ostwald at 18° and 25°. His work was not carried far enough to justify him in drawing any general conclusion.

Whetham[2] carried out a very careful piece of work for the purpose of comparing the ionization values obtained by the conductivity method with the results obtained by the freezing-point method. He used an elaborate piece of apparatus, and tried in every way to minimize the sources of error. He worked with several electrolytes at zero, and compared his values with those obtained at higher temperatures. He thinks that temperature has a slight effect on the amount of dissociation, the higher the temperature the less the dissociation.

E. Krannhals[3] carried out a piece of work with the same dilutions at different temperatures. He worked at temperatures ranging from 18° to 99°.4. He used hydrochloric acid, and several salts which are very good examples of strongly dissociated electrolytes. He calculated the temperature coefficients between 18° and 99°.4. As the dilution increases the temperature coefficient becomes greater. He also concluded that temperature has no effect on the amount of dissociation.

The subject of the influence of temperature on conductivity has been carefully and thoroughly worked out by many experimenters, but through rather narrow ranges of temperature. Grotrian,[1] and Kohlrausch and Grotrian[2] worked out the influence of temperature on conductivity, and also the temperature coefficients for sulphuric and hydrochloric acids, and several other electrolytes. Temperature coefficients for some of the more common salts have been determined by Freund,[3] Long,[4] and Booty.[5] Jahn[6] did a very extensive piece of work on the fatty acids. There is also a dissertation by Carl Deguisne,[7] of Strassburg, in which he has determined the temperature coefficient, in very dilute solutions, for a large number of electrolytes. Arrhenius[8] has done an interesting piece of work along this same line, for temperatures ranging from 18° to 52°.

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[1] Phil. Mag., **41**, 117.

[2] Ztschr. phys. Chem., **33**, 344.

[3] *Ibid.*, **5**, 250.

In all of the above work it was found that conductivity increases with the temperature. Also, that as the dilution increases the temperature coefficients of conductivity become greater. Deguisne concluded from his work that for salts there is an increase in the temperature coefficient with a rise in temperature, while for acids there is a decrease with a rise in temperature.

Introduction.

This piece of work was undertaken for the purpose of determining whether or not temperature has any influence on the dissociation of electrolytes, and, if so, the order of the magnitude of this influence. This work extends over a considerable range of temperatures, *viz.*, from 0° to 35°. We not only determined the percentage of dissociation at the respective temperatures, for the several dilutions of the electrolytes used, but also the temperature coefficient of conductivity for these temperatures.

The electrolytes used were hydrochloric, nitric, and sulphuric acids, potassium hydroxide, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, sodium nitrate, ammonium nitrate, potassium sulphate, and potassium permanganate.

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[1] Pogg. Ann., **151**, 390.

[2] *Ibid.*, **154**, 224.

[3] Wied. Ann., **7**, 47.

[4] *Ibid.*, **11**, 37.

[5] Ann. chim. phys., [6], **3**, 498.

[6] Ztschr. phys. Chem., **16**, 72.

[7] Inaugural Dissertation, Strassburg.

[8] Ztschr. phys. Chem., **4**, 96.

The percentage of dissociation for any dilution of any electrolyte at a given temperature, is the ratio of the molecular conductivity at that dilution to the maximum molecular conductivity of the electrolyte.

Apparatus.

The measurements of conductivity were made by the Kohlrausch method, using the wheatstone bridge, induction coil, and telephone. The Arrhenius type of cells was used. The electrodes were placed at such distances as would give good tone-minima, several cells being used with each substance. Wide electrodes were employed for the more concentrated solutions, and for the more dilute solutions the plates were placed close together. To avoid the error arising from the solubility of the glass at more elevated temperatures, porcelain cups were used for making the measurements at 35°. The temperatures selected were zero, that of the hydrant water which varied from time to time from 7° to 18°, 25°, and 35°. By means of the Ostwald thermoregulator the temperatures of the 25° and 35° baths were kept constant. The baths were kept stirred by fans driven by a gas-jet. The zero bath was prepared as follows: A glass battery jar was filled with pure, well-crushed ice, to which a little redistilled water was added. This was placed in a water-bath, the space between the two being filled with ice and water. The outer bath served to protect the inner bath from the warmer air of the room. The inner bath was stirred from time to time, while the cell containing the solution was immersed in the ice. The temperature was found always to remain within 0°.05 of zero. A constant stream of hydrant water was passed through a large vessel to obtain the temperature intermediate between 0° and 25°. After the stream had flowed for about an hour we found that the temperature remained very constant throughout the day, never varying more than 0°.1 during the time we were making the readings. The temperature would, of course, change considerably from day to day.

Solutions.

The flasks used were carefully calibrated for 20°, by the method devised by Morse and Blalock.[1] The pipettes were also carefully calibrated. The flasks and pipettes agreed with each other. The solutions were prepared at 20°, and generally standardized by analysis. Solutions of some of the salts, however, were made up by weight. Since the purity of the water used would have a marked effect on the results, the orordinary distilled water was redistilled successively from acid and alkaline potassium permanganate, employing a block-tin condenser. The method used was that described by Jones and Mackay.[2]

The conductivity of the water used in making up the solutions was determined, and the corresponding correction applied for each dilution above volume 32.

Conductivity Measurements.

The several dilutions were prepared by taking a measured volume from the original standard solution, and diluting to the desired volume in a measuring flask. To avoid the error resulting from the measurements of very small volumes, only the solutions up to volume 128 were made directly from the original mother-solution. This solution of volume 128 was used as the mother-solution for preparing the more dilute solutions up to volume 2048. Solution of volume 2048, prepared directly from solution of volume 128, was then used as a third mother-solution, and the still more dilute solutions prepared from this as the starting-point. The cell constants were determined very frequently. The constant for any cell used was found to vary but little during the entire year's work. All cells were standardized with a N/50 solution of potassium chloride. In each determination of conductivity, from three to five different resistances were used in the rheostat, the amount of resistance being so chosen that the readings on the bridge were always between 400 mm. and 600 mm.

Each result given is the average of from three to five conductivity measurements. The measurements of the conductivity of the solution were made; the solution was then stirred by quietly raising the electrodes several times. Fifteen or twenty minutes later the conductivity of the solution was again measured. This was a check on the first set of measurements.

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[1] This JOURNAL, **16**, 479.

[2] *Ibid.*, **19**, 83.

For the corrections in volume due to temperatures which were higher and lower than that at which the measuring apparatus was calibrated, we made use of data given by Schulze.[1] The change in volume of dilute solutions was taken to be the same as that of water. Instead of applying the corrections directly to the volume we applied them to the conductivity measurements.

Hydrochloric Acid.

The normal solution of hydrochloric acid was prepared by dissolving pure hydrochloric acid in redistilled water, and titrating against standard solutions of potassium and sodium hydroxides. The hydroxides used were standardized by titrating against sulphuric acid, which had been standardized gravimetrically by precipitation as barium sulphate. The conductivity measurements of Ostwald and Krannhals, at 15°, are given along with our own values for the purpose of comparison. Kohlrausch also determined the conductivity at 18°, but at different volumes. The following measurements were made:

v is the volume of the solution which contains a gram-molecular weight of the electrolyte, and μ_v the molecular conductivity at the temperature in question.

Krannhals' experimental work with hydrochloric acid was done at 18°. The values given in the table were obtained by transforming his values from 18° to 15°. This was done by using the temperature coefficients which we found between 15° and 25°. Krannhals' and Ostwald's values agree very well with our own.

By examining Table III. we see that temperature has practically no effect on the amount of dissociation. The temperature coefficient of conductivity of hydrochloric acid increases as the solution becomes more dilute.

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[1] Ztschr. anal. Chem., 21, 167.

Table I.—Molecular Conductivities of Hydrochloric Acid.

v.	μ_v 0°.	μ_v 15°.	μ_v 15°. (Krannhals.)	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
2	216.5	286.5	287.44	331.7	331.0	371.6
8	228.2	307.2	308.18	356.6	355.0	405.1
16	230.7	310.0	312.68	364.4	362.0	415.2
32	233.6	321.1	319.40	371.1	369.0	420.6
128	239.0	327.5	325.7	378.7	376.0	430.4
256	....	....	327.7	....	378.0	....
512	240.5	327.7		378.7		430.4
1024	240.6	327.7		378.7		430.4
2048	240.4	327.3		378.0		430.4
μ_∞	240.6	327.7		378.7		430.4

Table II.—Temperature Coefficients of Conductivity of Hydrochloric Acid.

v.	0°–15°.	15°–25°.	25°–35°.
2	4.67	4.52	3.99
8	5.27	4.94	4.85
16	5.29	5.44	5.08
32	5.83	5.00	4.95
128	5.90	5.12	5.17
512	5.81	5.10	5.17
1024	5.81	5.10	5.17
2048	5.79	5.07	5.24

Table III.—Dissociation of Hydrochloric Acid at Different Temperatures.

v.	0°.	15°.	25°.	35°.
2	89.9	87.4	87.6	86.3
8	94.8	93.7	94.2	94.1
16	95.9	94.6	96.2	96.5
32	97.1	98.0	98.0	97.7
128	99.3	99.9	100.0	100.0
512	100.0	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	99.8	100.0

Nitric Acid.

The solution was prepared and standardized in the same manner as the solution of hydrochloric acid—by titrating against standard solutions of potassium and sodium hydroxides. Kohlrausch's measurements for nitric acid were made at 18° and with different volumes, but by transforming his results to 13° and interpolating between his volumes we find that his measurements agree very closely with our own.

Nitric acid, like hydrochloric, is a very strong acid. It is almost completely dissociated at volume 128, and over 87 per cent at volume 2.

As the dilution increases the temperature coefficient also increases. The effect of temperature on dissociation is practically zero.

Table IV.—Molecular Conductivities of Nitric Acid.

v.	$\mu_v\ 0^\circ$.	$\mu_v\ 13^\circ$.	$\mu_v\ 25^\circ$.	$\mu_v\ 35^\circ$.
2	213.3	271.0	323.4	370.4
8	224.4	292.0	350.4	400.5
16	231.4	299.3	360.0	410.5
32	232.0	303.2	365.0	....
128	234.5	306.9	365.4	421.3
512	233.6	306.9	366.3	420.8
1024	235.6	307.0	368.0	421.3
2048	235.6	307.0	368.0	421.3
μ_∞	235.6	307.0	368.0	421.3

Table V.—Temperature Coefficients of Conductivity of Nitric Acid.

v.	0°–13°.	13°–25°.	25°–35°.
2	4.4	4.37	4.70
8	5.22	4.87	5.01
16	5.22	5.06	5.05
32	5.48	5.15	....
128	5.57	4.88	5.59
512	5.64	4.95	5.45
1024	5.49	5.08	5.33
2048	5.49	5.08	5.33

Table VI.—Dissociation of Nitric Acid at Different Temperatures.

v.	0°.	13°.	25°.	35°.
2	90.6	88.3	87.9	87.9
8	95.2	95.1	95.2	95.0
16	98.2	97.5	97.8	97.4
32	98.5	98.8	99.2	....
128	99.5	99.9	99.3	100.0
512	99.2	99.9	99.5	99.9
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Sulphuric Acid.

The normal solution of sulphuric acid was prepared in the same manner as that of hydrochloric acid and nitric acid. It was titrated against the normal solutions of potassium and sodium hydroxides. The following results were obtained:

Table VII.—Molecular Conductivities of Sulphuric Acid.

v.	μ_v 0°.	μ_v 15°.	μ_v 25°.	μ_v 35°.
2	277.3	346.0	390.0	464.0
8	306.2	391.0	425.9	490.0
16	321.7	410.0	449.8	535.0
32	350.8	445.4	490.0	590.6
128	400.7	508.1	582.8	684.8
512	449.8	571.6	675.0	760.0
1024	475.0	630.0	697.0	842.0
2048	488.3	643.5	705.8	853.0
4096	493.0	650.0	713.0	854.0
8192	495.0	650.0	713.0	856.0
16384	500.0	650.0	713.0	856.0
μ_∞	500.0	650.0	713.0	856.0

Table VIII.—Dissociation of Sulphuric Acid at Different Temperatures.

v.	0°.	15°.	25°.	35°.
2	55.5	53.2	54.7	54.2
8	61.2	60.2	59.7	57.2
16	64.3	63.1	63.1	62.5
32	70.2	68.5	68.7	69.0
128	80.1	78.2	81.7	80.0
512	90.0	87.9	94.7	88.8

v.	0°.	15°.	25°.	35°.
1024	95.0	96.9	97.7	98.4
2048	97.7	99.0	98.9	99.6
4096	98.6	100.0	100.0	99.8
8102	99.0	100.0	100.0	100.0
16384	100.0	100.0	100.0	100.0

We see from the table of molecular conductivities that we do not have complete dissociation with sulphuric acid until a volume of 4096 is reached.

Potassium Hydroxide.

The normal solution of potassium hydroxide by alcohol was prepared by titrating against a standard solution of sulphuric acid. The results obtained by Kohlrausch at 18° are published for the sake of comparison.

From the table of conductivities we see that our values agree very well with those of Kohlrausch at the same temperature. The measurement of the conductivity of potassium hydroxide was at first rather difficult. We then let very strong potassium hydroxide remain in the cells for several days, and then added strong sulphuric and hydrochloric acids. After washing the cells out thoroughly they were standardized, and we experienced no further trouble with the more concentrated solutions. However, for the dilutions above volume 128 the conductivities would change slightly after the solutions had stood several hours, the more dilute the solution the more rapid the change. This change was very much more rapid while the solution was in the cell than while standing in the glass bottles, and was doubtless due in part to the absorption of carbon dioxide from the air. The method pursued for volumes above 128 was to bring the solution to the desired temperature before placing it in the cells. The measurements were then made as quickly as possible. The electrodes were then lifted out of the cell and the temperature of the solution taken. Each of the results given for dilutions above volume 128 are the mean of measurement of six to ten separately prepared solutions. For each solution three or four readings were made, using different resistances. The conductivities of the solutions were always measured immediately after they were prepared, and never after standing two or three hours. Complete dissociation was reached at volume 256. The molecular conductivity of solutions whose dilution was greater than 700 always decreased slightly with increase in dilution.

The same fact is brought out in Kohlrausch's results. Above a volume of 500 there is a slight decrease in conductivity.

The temperature coefficients are less regular for potassium hydroxide than for the acids studied. This is doubtless due to the greater difficulty experienced in making accurate conductivity measurements.

Table IX.—Molecular Conductivities of Potassium Hydroxide.

v.	μ_v 0°.	μ_v 18°.	μ_v 18°. (Kohlrausch.)	μ_v 25°.	μ_v 35°.
1	113.5	171.8	171.8	185.2	214.8
2	118.4	184.1	184.1	197.9	227.9
8	122.8	194.0	(194.9)	201.5	232.2
16	125.3	200.0	202.14	212.0	247.5
32	127.6	205.0	207.55	223.0	256.9
128	133.7	212.4	....	226.0	257.7
256	134.0	214.0	....	226.0	258.0
512	134.0	214.0	....	226.0	258.0
500	....	....	214.0	....	....
μ_∞	134.0	214.0		226.0	258.0

Table X.—Temperature Coefficients of Conductivity of Potassium Hydroxide.

v.	0°–18°.	18°–25°.	25°–35°.
1	3.2	....	2.96
2	3.65	....	3.00
8	3.96	....	3.07
16	4.15	....	3.55
32	4.30	....	3.39
128	4.37	....	3.17
256	4.44	....	3.20
512	4.44	....	3.20

Table XI.—Dissociation of Potassium Hydroxide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	84.7	80.3	81.9	83.3
2	88.4	86.0	87.6	88.3
8	91.6	90.7	89.2	90.0
16	93.6	93.5	93.8	95.9
32	95.2	95.8	98.7	99.6
128	99.8	99.3	100.0	100.0
256	100.0	100.0	100.0	100.0
512	100.0	100.0	100.0	100.0

Sodium Hydroxide.

A normal solution of sodium hydroxide was prepared in the same manner as that of potassium hydroxide. Pure samples of sodium hydroxide, by alcohol, were dissolved in redistilled water and titrated against the same standard sulphuric acid that was used for the potassium hydroxide. Kohlrausch's measurements at 18° are also published in the following table:

The same difficulties were encountered in working with sodium hydroxide that were met with in the case of potassium hydroxide. The method pursued for making the conductivity measurements of sodium hydroxide was the same as used with potassium hydroxide. In both cases difficulty was encountered especially in the more dilute solutions.

Our measurements agree very well with those obtained by Kohlrausch for the same temperature. At about volume 200 there is complete dissociation. Kohlrausch found that after volume 166.7 was reached the molecular conductivities gradually decreased. We noticed the same phenomenon in the very dilute solutions. The dilutions were made as with the acids. In both of the hydroxides, temperature has little or no effect on the amount of dissociation. The temperature coefficient of conductivity however, increases with the dilution, but only slightly. The coefficients show marked irregularities, which are doubtless due to experimental errors.

Table XII.—Molecular Conductivities of Sodium Hydroxide.

v.	μ_v 0°.	μ_v 18°.	μ_v 18°. (Kohlrausch.)	μ_v 25°.	μ_v 35°.
1	97.5	147.0	149.0	162.5	189.4
2	104.8	163.0	163.0	177.0	206.5
8	115.0	170.0	168.2	195.0	228.7
16	117.0	174.0	173.2	200.2	232.8
32	121.4	180.0	179.4	205.3	234.5
128	124.0	187.0	....	212.0	244.7
256	125.0	188.0	....	212.0	242.0
512	125.0	188.0	....	210.0	240.0
μ_∞	125.0	188.0	188.0	212.0	244.7

Table XIII.—Temperature Coefficients of Conductivity of Sodium Hydroxide.

v.	0°–18°.	18°–25°.	25°–35°.
1	2.78	....	2.69
2	3.23	....	2.95
8	3.06	3.57	3.37
16	3.17	3.71	3.26
32	3.26	3.61	2.92
128	3.50	3.57	3.27
256	3.50	3.43	3.00
512	3.50	3.14	3.00

Table XIV.—Dissociation of Sodium Hydroxide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	78.0	78.2	76.6	77.4
2	83.8	86.7	83.5	84.4
8	92.0	90.4	92.0	93.5
16	93.6	92.5	94.4	95.1
32	97.1	95.7	96.8	95.8
128	99.2	99.5	100.0	100.0
256	100.0	100.0	100.0	98.9
512	100.0	100.0	99.1	98.1

Potassium Chloride.

This salt was recrystallized four times from distilled water, then from redistilled water. It was dried by heating for two days at 150°, then placed in a desiccator until used. The solutions were made up by weight. A gram-molecular weight was dissolved in water and diluted to 1 liter. The conductivity of this salt had been measured by several. Ostwald's and Wood's values are published along with our own for the sake of comparison. Several others have worked at 18°, but their values would have to be transformed from 18° to 7°.1 and also interpolated for volume.

Most of the results obtained by Wood and Ostwald are a little lower than our values. Table XVII shows an increase in the temperature coefficient as the dilution increases. It will be seen that the temperature coefficient for the same volume becomes larger in each case as we pass to higher temperatures. Potassium chloride is completely dissociated at a volume of 1024. The amount of dissociation is practically independent of temperature.

Table XV.—Molecular Conductivities of Potassium Chloride.

v.	μ_v 0°.	μ_v 0°. (Wood.[1])	μ_v 7°.1.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	58.5	61.1	72.4	103.0		121.4
2	62.0	62.49	74.6	108.0		129.0
8	66.7	66.47	76.0	118.7		141.4
16	70.0	68.70	83.8	122.6		147.5
32	72.0	70.66	88.0	128.4	127.3	152.0
128	75.0	73.90	91.0	134.9	133.6	164.3
1024	78.0	76.35	95.0	139.8	139.9	169.0
2048	78.8	....	95.0	139.2	....	169.0
μ_∞	78.8		95.0	139.8		169.0

Table XVI.—Temperature Coefficients of Conductivity of Potassium Chloride.

v.	0°–7°.1.	7°.1–25°.	25°–35°.
1	1.96	1.71	1.84
2	1.78	1.86	2.10
8	1.31	2.38	2.27
16	1.94	2.17	2.49
32	2.25	2.26	2.36
128	2.25	2.45	2.94
1024	2.39	2.50	2.92
2048	2.28	2.47	2.98

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[1] Phil. Mag., 41, 118.

Table XVII.—Dissociation of Fotassium Chloride at Different Temperatures.

v.	0°.	7°.1.	25°.	35°.
1	74.2	76.2	73.7	71.8
2	78.7	78.7	78.5	76.3
8	84.6	84.0	80.0	83.7
16	88.8	88.2	88.2	87.3
32	91.4	92.6	92.6	90.0
128	95.1	95.8	95.8	97.2
1024	99.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Potassium Bromide.

A comparatively pure sample of potassium bromide was recrystallized three times. The flame test showed no trace of impurity. This salt was then dried by heating in an air-bath for twelve hours, at a temperature of 105°. It was then placed in a desiccator, where it remained until used. The solution was prepared by dissolving 59.555 grams of the salt in water in a liter measuring flask, and diluting to volume.

Krannhals, Ostwald, and Kohlrausch have determined the conductivity of potassium bromide at 18° and 25° for several dilutions. In the few cases in which our volumes and temperatures are the same their results are given with our own.

The measurements at 18° were made at different times and at different temperatures, as can be seen from the table. The measurements were all transformed to 18° by means of the temperature coefficients. Our results agree very well with those of Kohlrausch and Ostwald. Those of Krannhals are, in general, a little lower. There is a gradual increase in the value of the temperature coefficient as the dilution increases. As we pass from 0° to 30° there is a gradual rise in the value of the temperature coefficient, but there is a drop from 30° to 35°. The amount of dissociation remains perfectly constant as the temperature increases from 0° to 35°. For volume 2, temperature 35°, the dissociation found is a little low, but this is in all probability due to experimental error. We are justified in concluing that temperature has little or no effect on the amount of dissociation.

Table XVIII.—Molecular Conductivities of Potassium Bromide.

v.	μ_v 0°.		μ_v 18°.	μ_v 18°. (Krannhals.)	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 30°.	μ_v 35°.
2	66.4	98.2(17°.5)	99.2	98.2	113.2		123.1	129.4
8	69.3	105.3(17°.6)	106.1	105.7	120.4		132.6	142.2
16	73.4	109.9(17°.7)	110.1	110.0	125.6		138.9	149.3
32	75.1	......	115.1	113.0	129.0	128.7	141.6	153.2
128	77.5	119.0(17°.8)	120.1	117.0	137.0	136.1	150.2	160.4
512	79.9		123.0		141.0	140.8	158.1	170.6
1024	84.2		125.0		143.4	141.2	160.2	173.2
2048	84.2		125.0		143.4	....	160.2	173.2
μ_∞	84.2		125.0		143.4		160.2	173.2

Table XIX.—Temperature Coefficients of Conductivity of Potassium Bromide.

v.	0°–18°.	18°–25°.	25°–30°.	30°–35°.
2	1.82	2.00	1.98	....
8	2.04	2.04	2.44	....
16	2.04	2.21	2.66	2.08
32	2.22	2.00	2.52	2.32
128	2.37	2.41	2.64	2.04
512	2.40	2.57	3.42	2.50
1024	2.27	2.63	3.36	2.60
2048	2.27	2.63	3.36	2.60

Krannhals found the temperature coefficient between 18° and 99°.4 to be:

v.	18°–99°.4.
1	1.97
16	2.23

Table XX.—Dissociation of Potassium Bromide at Different Temperatures.

v.	0°.	18°.	25°.	30°.	35°.
2	78.8	79.3	78.9	76.8	74.7
8	82.3	84.9	84.0	82.8	82.1
16	87.2	88.1	87.6	86.7	86.2
32	89.2	92.1	90.0	88.4	88.5
128	92.0	96.1	95.5	93.8	92.6
512	94.9	98.4	98.3	98.7	98.5
1024	100.0	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0	100.0

Potassium Iodide.

The pure potassium iodide was dried by allowing it to remain in the desiccator for a long time. The solution was prepared as with potassium bromide and chloride. Kohlrausch and Ostwald have measured the conductivities at 18° and 25°. Kohlrausch did not work at the same volumes which we employed, consequently his values were obtained by interpolation. Ostwald's values for 25° agree very closely with our own, but Kohlrausch's values are in some cases a little higher. We find the same general rule to hold for dissociation and temperature coefficients, as has been observed with the preceding compounds.

Table XXI.—Molecular Conductivities of Potassium Iodide.

v.	μ_v 0°.	μ_v 18°. (Kohlrausch.)	μ_v 18°.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	59.8	96.8	94.0	108.1		126.6
2	62.4	99.7	98.8	111.5		132.0
8	66.3	105.1	104.0	120.1		142.3
16	70.6	108.8	107.2	122.9		146.8
32	72.9	112.0	113.7	128.9	128.5	155.0
128	76.4		116.3	135.0	135.4	159.6
512	78.0		119.0	140.0	139.6	166.0
1024	78.0		120.8	141.0	140.7	166.0
2048	78.0		121.0	141.0	....	166.7
μ_∞	78.0		121.0	141.0		166.7

Table XXII.—Temperature Coefficients of Conductivity of Potassium Iodide.

v.	0°–18°.	18°–25°.	25°–35°.
1	1.90	2.01	1.85
2	2.07	1.81	2.05
8	2.16	2.30	2.22
16	2.12	2.24	2.39
32	2.17	2.17	2.61
128	2.11	2.67	2.46
512	2.28	3.00	2.60
1024	2.38	2.88	2.50
2048	2.39	2.86	2.57

Table XXIII.—Dissociation of Potassium Iodide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	76.7	77.7	76.7	76.0
2	80.0	81.7	79.1	79.2
8	85.0	85.9	85.2	85.4
16	90.5	88.6	87.2	88.1
32	93.5	94.0	91.4	93.0
128	97.9	96.1	95.9	95.4
512	100.0	98.3	99.3	99.6
1024	100.0	99.9	100.0	99.6
2048	100.0	100.0	100.0	100.0

Potassium Nitrate.

The potassium nitrate used was the product of the fourth fractional crystallization of a very good sample of the salt.

The flame test showed no sodium. The nitrate was dried in an air-bath by heating to 120° for two days. It was then left in a desiccator for three days. A normal solution was prepared by weight. The conductivity of this salt has been determined by Kohlrausch at 18°, Ostwald at 25°, and Krannhals at from 18° to 99°.4.

By transforming their values from 18° to 7° they agree very well with our values. Ostwald's values are given :

Table XXIV.—Molecular Conductivities of Potassium Nitrate.

v.	μ_v 0°.	μ_v 7°.5.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	50.8	61.5	85.0		100.1
2	53.2	....	95.0		113.4
8	60.1	75.0	107.0		128.3
16	65.0	81.2	116.3		140.1
32	70.3	82.8	118.0	120.1	144.0
128	71.6	86.7	128.0	128.0	155.2
512	72.0	93.0	131.0	132.9	157.5
1024	73.6	93.0	130.8	133.0	157.4
2048	73.6	93.0	131.0		158.0
μ_∞	73.6	93.0	131.0		158.0

Table XXV.—Temperature Coefficients of Conductivity of Potassium Nitrate.

v.	0°–7°.5.	7°.5–25°.	25°–35°.
1	1.43	1.34	1.51
2	....	....	1.84
8	1.99	1.83	2.13
16	2.02	2.00	2.38
32	....	2.01	2.60
128	2.01	2.36	2.72
512	2.80	2.17	2.65
1024	2.59	2.16	2.66
2048	2.59	2.17	2.70

Table XXVI.—Dissociation of Potassium Nitrate at Different Temperatures.

v.	0°.	7°.5.	25°.	35°.
1	69.0	66.1	64.9	63.4
2	72.3	....	72.5	71.8
8	81.7	80.6	81.7	81.2
16	88.3	87.3	88.8	88.6

v.	0°.	7°.5.	25°.	35°.
32	95.5	89.0	90.0	91.1
128	97.3	93.2	97.7	98.1
512	97.7	100.0	100.0	99.7
1024	100.0	100.0	99.9	99.6
2048	100.0	100.0	100.0	100.0

The molecular conductivity at 25° agrees fairly well with Ostwald's values. His value for volume 1024 is a little higher than the value which we obtained. We took Krannhals' values for 50° and transformed them to 35°, and found them to agree very closely with our own. The temperature coefficient for potassium nitrate, like the temperature coefficient of the substances thus far studied, increases with increase in dilution. We also notice an increase in the temperature coefficient as we pass from 0° to 35°. The dissociation of potassium nitrate is independent of temperature. The same volumes give practically the same dissociation at different temperatures, except in one or two cases, which seem to be due to some experimental error.

Sodium Nitrate.

The salt was purified by recrystallization. The flame test showed no trace of potassium. It was dried by heating in an air-bath for two days at 120°, and kept in a desiccator until used. The solution was prepared from the pure, dry salt by dissolving a gram-molecular weight in water and diluting to 1 liter. The conductivities of sodium nitrate, as obtained by Krannhals and Ostwald, are also given in the following table.

Krannhals' values were transformed from 18° to 13°. This was done by means of the temperature coefficients found. His results are almost exactly the same as our own. Our values for 25° also agree very closely with those of Ostwald. We notice in sodium nitrate, as in the compounds thus far dealt with, an increase in the temperature coefficients with an increase in dilution. We also notice an increase in the temperature coefficient as we pass from 0° to 35°. Temperature has little or no influence on dissociation.

Table XXVII.—Molecular Conductivities of Sodium Nitrate.

v.	μ_v 0°.	μ_v 13°. (Krannhals.)	μ_v 13°.	μ_v 25°.	μ_v 25°. (Ostwald).	μ_v 35°.
1	40.3	55.1	55.9	70.4		83.8
2	44.9	62.7	62.9	78.7		94.6
8	50.5	71.3	71.0	91.0		108.8
16	53.6	75.5	75.0	97.4		116.5
32	58.2	78.7	79.0	101.7	101.5	122.3
128	61.8	82.1	85.0	108.6	107.6	130.2
512	63.6		87.0	111.5	112.0	135.8
1024	64.0		90.5	113.7	112.7	137.4
2048	64.7		90.9	113.7		138.0
μ_∞	64.7	90.0	90.9	113.7		138.0

Table XXVIII.—Temperature Coefficients of Conductivity of Sodium Nitrate.

v.	0°–13°.	13°–25°.	25°–35°.
1	1.20	1.21	1.34
2	1.36	1.34	1.59
8	1.58	1.67	1.78
16	1.65	1.87	1.91
32	1.58	1.89	2.06
128	1.78	1.97	2.16
512	1.80	2.04	2.43
1024	2.04	1.93	2.37
2048	2.01	1.90	2.43

Table XXIX.—Dissociation of Sodium Nitrate at Different Temperatures.

v.	0°.	13°.	25°.	35°.
1	62.3	61.5	61.9	60.7
2	69.4	69.2	69.2	68.5
8	78.0	78.1	80.0	78.8
16	82.8	82.5	85.7	84.4
32	89.9	86.9	89.4	88.6
128	95.5	93.5	95.5	94.3
512	98.3	95.7	98.1	98.4
1024	98.9	99.6	100.0	99.6
2048	100.0	100.0	100.0	100.0

Ammonium Nitrate.

The salt was recrystallized several times. It was dried in an air-bath and then allowed to remain in a desiccator until used. The solution was prepared by weighing 80.12 grams of the salt, dissolving it in pure water in a liter flask, and diluting to the mark. The conductivity for ammonium nitrate was determined by Kohlrausch for very concentrated solutions at 18°.

Caldwell[1] determined, in this laboratory, the conductivity of ammonium nitrate at 25°.

Table XXX.—Molecular Conductivities of Ammonium Nitrate.

v.	μ_v 0°.	μ_v 9°.	μ_v 25°.	μ_v 35°.
1	55.3	67.4	93.9	111.7
2	58.3	73.2	101.0	....
4	61.2	77.7	107.0	127.8
10	64.3	82.7	114.5	137.2
20	68.1	86.8	119.6	142.9
40	69.6	88.3	123.5	148.4
100	70.2	90.0	126.8	152.2
200	73.7	93.2	129.9	155.3
400	71.3	94.9	131.7	164.1
1000	76.8	100.7	137.2	173.6
2000	78.0	99.0	137.8	170.8
μ_∞	78.0	100.7	137.8	173.6

Table XXXI.—Temperature Coefficients of Conductivity of Ammonium Nitrate.

v.	0°–9°.	9°–25°.	25°–35°.
1	1.34	1.66	1.78
2	1.66	1.75	....
4	1.83	1.83	2.08
10	2.04	1.99	2.27
20	2.08	2.05	2.33
40	2.08	2.20	2.47
100	2.20	2.30	2.54
200	2.17	2.29	2.54
400	2.62	2.30	3.24
1000	2.66	2.28	3.64
2000	2.33	2.42	3.30

[1] This Journal, 25, 349.

Table XXXII.—Ammonium Nitrate, Dissociation at Different Temperatures.

v.	0°.	9°.	25°.	35°.
1	70.9	66.9	68.1	64.4
2	74.8	72.7	73.3	....
4	78.1	77.2	77.7	73.6
10	82.0	82.1	83.1	89.0
20	87.3	86.2	86.8	82.3
40	89.3	87.7	89.6	85.5
100	90.0	89.4	92.0	87.7
200	94.5	92.6	94.3	89.5
400	91.4	94.2	95.6	94.5
1000	98.4	100.0	99.6	100.0
2000	100.0	98.3	100.0	98.4

We have in this case, as in the other cases, a gradual increase in the temperature coefficient as the dilution is increased. The temperature coefficient in a few cases seems to be a little higher than it should be. This is undoubtedly due to experimental error. The temperature coefficient is a little larger for the higher temperature than for the lower. We notice that in two cases the dissociation is complete at volume 1000, and is a little lower for volume 2000. The percentage of dissociation is very nearly the same at the different temperatures.

Potassium Sulphate.

The potassium sulphate was recrystallized four times. The flame showed no trace of sodium. It was heated for two days in an air-bath at 150° and allowed to remain in a desiccator until used. The solution was prepared by dissolving one-half of a gram-molecular weight of potassium sulphate in a liter flask and diluting to the mark. This solution had a volume of two.

Table XXXIII.—Molecular Conductivities of Potassium Sulphate.

v.	μ_v 0°.	μ_v 18°.	μ_v 25°.	μ_v 25°. (Walden.)	μ_v 35°.
2	86.8	133.4	150.7		175.7
8	103.9	160.1	181.7		218.6
16	113.6	174.7	196.2		235.6

v.	$\mu_v\ 0^\circ$	$\mu_v\ 18$.	$\mu_v\ 25^\circ$.	$\mu_v\ 25^\circ$. (Walden.)	$\mu_v\ 35$.
32	122.7	183.0	207.1		254.4
128	138.4	210.5	246.4	246.0	294.7
512	148.1	231.9	266.3	265.4	313.3
1024	157.9	243.8	274.4	272.8	326.3
2048	160.2	247.2	276.0	278.6	330.0
4096	160.2	247.2	276.0		330.0
μ_∞	160.2	247.2	276.0		330.0

Table XXXIV.—Temperature Coefficients of Conductivity of Potassium Sulphate.

v.	0°–18°.	18°–25°.	25°–35°.
2	2.58	2.47	2.50
8	3.12	3.09	3.69
16	3.39	3.07	3.93
32	3.35	3.44	3.73
512	4.65	4.91	4.70
1024	4.77	4.37	5.19
2048	4.77	4.11	5.40
4096	4.84	4.11	5.40

Table XXXV.—Dissociation of Potassium Sulphate at Different Temperatures.

v.	0°.	18°.	25°.	35°.
2	54.2	53.9	54.6	53.2
8	64.8	64.7	65.8	66.2
16	70.9	70.6	71.1	71.4
32	76.6	74.0	75.0	77.1
128	86.3	85.2	89.3	89.3
512	92.4	93.8	96.5	94.9
1024	98.5	98.6	99.4	98.9
2048	100.0	100.0	100.0	100.0
4096	100.0	100.0	100.0	100.0

Potassium Permanganate.

The potassium permanganate used was the product of the second fractional crystallization of a comparatively pure sample of the salt. It was dried and standardized by titrating against a standard solution of oxalic acid.

The conductivities of the more concentrated solutions were not measured, since the oxide would separate out on the electrodes.

Table XXXVI.—Molecular Conductivities of Potassium Permanganate.

v.	μ_v 0°.	μ_v 10°.3.	μ_v 25°.	μ_v 35°.
10.9	59.8	79.7	108.0	129.1
21.8	63.6	82.7	111.0	135.7
43.6	66.0	87.0	115.4	138.4
87.2	67.0	87.3	116.9	140.7
218.0	68.2	89.7	121.0	145.3
872.0	68.7	90.0	121.0	146.0
2180.0	68.0	89.0	121.0	144.0
μ_∞	68.7	90.0	121.0	146.0

Table XXXVII.—Temperature Coefficients of Conductivity for Potassium Permanganate.

v.	0°–10°.3.	10°.3–25°.	25°–35°.
10.9	1.93	1.92	2.11
21.8	1.86	1.93	2.47
43.6	2.04	1.93	2.30
87.2	1.97	2.03	2.38
218.0	2.09	2.12	2.43
872.0	2.07	2.11	2.50
2180.0	2.04	2.11	2.30

Table XXXVIII.—Dissociation of Potassium Permanganate at Different Temperatures.

v.	0°.	10°.3.	25°.	35°.
10.9	87.1	88.6	89.2	88.4
21.8	92.6	91.9	91.7	92.9
43.6	96.1	96.6	95.4	94.8
87.2	97.5	97.7	96.6	96.4
218.0	99.3	99.7	100.0	99.5
872.0	100.0	100.0	100.0	100.0
2180.0	99.0	98.9	100.0	98.6

The molecular conductivities for volume 2180 are a little lower at each temperature, except 25°, than the results for volume 872. This salt is not very soluble in water, and yet we have practically complete ionization at volume 218.

Here, again, we find the same phenomena that have appeared in the preceding cases.

Conclusion.

From the results obtained in this investigation we feel justified in concluding that the temperature coefficient of conductivity increases as the volume increases for acids, bases, and salts. For the salts the temperature coefficient increases as the temperature increases, but for the acids and bases there is so little change that we cannot say whether there is any effect or not.

Temperature does not affect, to any appreciable extent, the amount of dissociation, which is the most important result of this investigation.

This confirms the conclusion drawn a number of years ago, by one of us,[1] from a piece of work done by the freezing-point method. Jones determined, through a wide range of dilutions, the amount of dissociation of a number of acids, bases, and salts, and compared his results with those of Kohlrausch obtained by the conductivity method. The general agreement between the two sets of values is unmistakable. Since the one was obtained at a temperature slightly below zero, and the other at 18°, the temperature coefficient of dissociation must have a very small value.

The temperature coefficient of conductivity is, on the other hand, very large, and a positive quantity. Since conductivity is due to the number of ions present and the velocity with which they move, the effect of increase in temperature might be either to increase the number of ions present, or their velocity, or to increase both. But since it is shown that rise in temperature does not increase, appreciably, the number of ions present, it follows that the influence of temperature on conductivity is to affect the velocities with which the ions move.

Further work along this line is now in progress in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
June, 1901.

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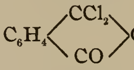
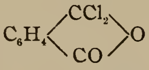
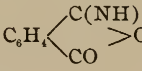
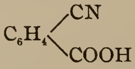
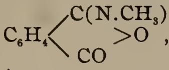
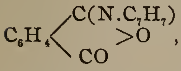
[1] Jones: Ztschr. phys. Chem., **2**, 110, 529; **12**, 623.

ACTION OF AROMATIC AMINES UPON PHTHALYL CHLORIDE AT DIFFERENT TEMPERATURES.

BY M. KUHARA AND M. FUKUI.

Some years ago one of us[1] observed the simultaneous formation of phthalimide and its isomeride by treating phthalyl chloride with aqueous ammonia, and offered a possible explanation of the formation of such an isomeride in these words:[2] "From the knowledge so far gained it seemed as though this substance must be regarded as an isomeride of phthalimide. According to Von Gerichten[3] it appears probable that phthalyl chloride is either  $C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O$ or a mixture of this substance with the normal chloride. If this view is correct, the formation of a substance isomeric with phthalimide might easily be accounted for. The action of ammonia upon a substance of the formula  $C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O$ might give rise to a product of the formula  $C_6H_4\left\langle\begin{matrix}C(NH)\\CO\end{matrix}\right\rangle O$, which would be isomeric with phthalimide."

Afterwards Allendorf[4] obtained the same substance by repeating the process proposed by one of us, but he thinks that it may be *o*-cyanobenzoic acid,  $C_6H_4\left\langle\begin{matrix}CN\\COOH\end{matrix}\right.$, which was found to change to ordinary phthalimide at a higher temperature.

Auger[5] states that he has obtained unsymmetrical phthalimide from unsymmetrical phthalamide formed from phthalyl chloride by treating with an excess of aqueous ammonia. According to Hoogewerff and Van Dorp's[1] experiments, however, phthalimide and phthalamide have the symmetrical formulas. But they state[2] that they have succeeded in preparing two substituted unsymmetrical phthalimides, namely phthalomethylisoimide,  $C_6H_4\left\langle\begin{matrix}C(N.CH_3)\\CO\end{matrix}\right\rangle O$, and phthalobenzylisoimide,  $C_6H_4\left\langle\begin{matrix}C(N.C_7H_7)\\CO\end{matrix}\right\rangle O$, by treating phthalomethylamic acid and phthalobenzylamic acid with acetyl chloride, respectively.

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[1] This JOURNAL, 3, 26.

[2] *Ibid.*

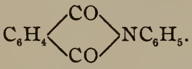
[3] Ber. d. chem. Ges., 13, 47.

[4] *Ibid.*, 24, 2348.

[5] Ann. chim. phys., (6), 22, 289.

Now, in order to determine whether a series of such substances of unsymmetrical imidic nature can really exist, the authors have lately undertaken the study of the action of aromatic amines upon phthalyl chloride at different temperatures.

Action of Aniline upon Phthalyl Chloride.

s-Phenylphthalimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5$. — Ethereal solutions of phthalyl chloride (1 mol.) and aniline (3 mols.) were allowed to act upon each other at ordinary temperature. The precipitate, which is formed immediately after mixing the two substances, was filtered and washed successively with hydrochloric acid, ammonia, and water. The substance thus obtained was purified by repeated recrystallization from alcohol.

It crystallizes in prismatic needles and is insoluble in water, and moderately soluble in hot glacial acetic acid and alcohol. Its melting-point is 203°. This substance is identical with phthalanil prepared by other methods by Laurent and Gerhardt,[3] and also by Doebner,[4] Piutti,[5] and Michael and Palmer.[6] It seems to possess the symmetrical structure as commonly accepted, as will be explained afterwards. We therefore call it *s*-phenylphthalimide.

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[1] Rec. trav. chim., **11**, 84.

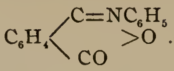
[2] *Ibid.*, **13**, 93.

[3] Jsb. Chem., 1847–48, 605.

[4] Ann. Chem. (Liebig), **210**, 267.

[5] Ber. d. chem. Ges., **16**, 1323.

[6] This JOURNAL, **9**, 202.

a-Phenyl Phthalimide,  $C_6H_4\left\langle\begin{matrix}C{=}NC_6H_5\\ CO\end{matrix}\right\rangle O$.—A moderately dilute ethereal solution of phthalyl chloride, cooled to —10°, was cautiously added drop by drop to an ethereal solution of aniline (3 mols.) cooled to the same temperature. The reaction immediately took place and a white crystalline substance was precipitated after each addition, but it was found to be most advantageous not to allow the temperature of the mixture to rise higher than —5° throughout the course of the experiments. The precipitate, now separated from the liquid by filtration, was thoroughly washed with hydrochloric acid, ammonia, and water, successively, and then repeatedly treated with boiling alcohol to free it from some *s*-phenylphthalimide formed simultaneously and mixed with it. The residue or less soluble portion of the precipitate was dissolved in hot glacial acetic acid and allowed to crystallize. In order to get it in pure state it was found best to recrystallize it from a large quantity of alcohol.

The substance thus prepared consists of groups of white, microscopic, acicular crystals. It is insoluble in water, slightly soluble in alcohol, and readily in hot glacial acetic acid. Its melting-point is 218°, as determined by the capillary-tube method, but 235° as found by Kuhara and Chikashigé's[1] method. The substance dried over sulphuric acid was analyzed and the results are given below:

I. 0.3760 gram substance gave 0.0243 gram nitrogen.
II. 0.2760 gram substance gave 0.0178 gram nitrogen.
III. 0.3950 gram substance gave 0.0254 gram nitrogen.

	Calculated for $C_{14}H_9O_2N$.		Found.	
		I.	II.	III.
N	6.28	6.44	6.45	6.43

From the results of analysis, the substance must be considered to be isomeric with ordinary phenylphthalimide or *s*-phenylphthalimide, and we call this new compound *a*-phenylphthalimide from its unsymmetrical structure, as will be explained afterwards.

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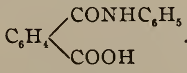
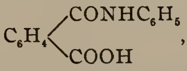
[1] This JOURNAL, **23**, 230.

The substance was observed to change to its isomeride or *s*-phenylphthalimide at a high temperature as when it is heated in a sealed tube suspended in *o*-xylene at 140°, it passed into solution and again separated out in the form of fine needles which were found to melt at 203° (melting-point of *s*-phenylphthalimide). The substance, perfectly dried over calcium chloride under reduced pressure, was found to change entirely to *s*-phenylphthalimide when heated quickly over a flame in a test-tube, but when moist it decomposed partly into aniline and phthalic anhydride. We often noticed the evolution of the characteristic smell of isonitril by simply heating the substance in an oil-bath above 150°.

In order further to examine the action of water upon the substance, it was heated with water in a sealed tube at 140°. After fourteen hours it was found to have changed entirely to *s*-phenylphthalimide, aniline, and phthalic acid. On heating the substance with alcoholic ammonia, part of it decomposed into aniline and ammonium phthalate and a part remained unchanged. This is one of the means of distinguishing *a* phenylphthalimide from *s*-phenylphthalimide, the latter being transformed to ammonium phenylphthalamate, under similar treatment, as shown by Laurent and Gerhardt.[1]

Phenylphthalamic Acid,  $C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right.$. — The acid usually known as phenylphthalamic acid, the commonly accepted formula of which is  $C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right.$, was first prepared by Laurent and Gerhardt[2] by boiling phthalanil with alcoholic ammonia. We found, however, that it can readily be formed in the form of the barium salt by boiling *s*-phenylphthalimide with baryta water and removing the excess of baryta by means of carbon dioxide. On concentrating the filtrate the barium salt crystallized out and the crystals dried over sulphuric acid were analyzed.

0.1934 gram substance gave 0.0445 gram barium.

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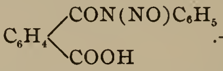
[1] Jsb Chem., 1847-1848, p. 605.

[2] *Ibid.*

	Calculated for $(C_{14}H_{10}O_3)_2Ba$.	Found.
Ba	22.8	22.8

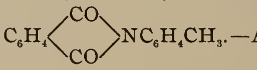
The free acid can readily be obtained by adding hydrochloric acid to the solution of its barium salt, when it is precipitated in the form of fine crystals. This acid is not formed at all from *a*-phenylphthalimide by similar treatment with either alcoholic ammonia or baryta water.



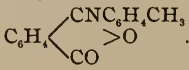
Oxyphthalylnitrosoaniline, $C_6H_4\begin{cases}CON(NO)C_6H_5\\COOH\end{cases}$.—Upon 10 grams of phenylphthalamic acid, suspended in 100 cc. of ether, nitrous acid gas was allowed to act. It gradually passed into solution, and after seven hours pale-yellow, fine crystals separated out. They were filtered, well washed with ether, and dried over calcium chloride.

It is easily soluble in water and alcohol and less in ether. It gives Liebermann's nitroso reaction with phenol and sulphuric acid; when heated it explodes, as also by percussion. On boiling with water, it was found to yield chiefly phenol and phthalic acid with evolution of nitrogen, and at the same time some nitrous acid was evolved and some *s*-phenylphthalimide formed. On standing in the air, and even under a desiccator, it gradually decomposes. Owing to the unstable character of the substance, we were not able to analyze it.

Action of Orthotoluidine upon Phthalyl Chloride.



s-Orthotolylphthalimide, $C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_4CH_3$.—A number of years ago this compound was prepared by Fröhlich[1] by heating orthotoluidine and phthalic anhydride together; and lately one of us[2] obtained the same substance on heating orthotoluidine and phthalyl chloride together, and already communicated to this JOURNAL the results of studies which support the view that it has the symmetrical structure.



a-Orthotolylphthalimide, $C_6H_4\begin{cases}CNC_6H_4CH_3\\ \quad >O\\CO\end{cases}$.—This new substance was formed from orthotoluidine and phthalyl chloride under conditions similar to those observed at the formation of *a*-phenylphthalimide. It is insoluble in water and readily soluble in hot alcohol. It crystallizes in beautiful silky needles from hot alcohol. Its melting-point is 201°. The crystals, dried over calcium chloride, were analyzed:

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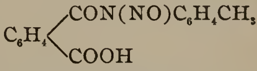
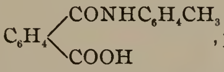
[1] Ber. d. chem. Ges., 17, 2679.

[2] This JOURNAL, 9, 52.

I. 0.2530 gram substance gave 0.0134 gram nitrogen.
II. 0.3373 gram substance gave 0.0188 gram nitrogen.
III. 0.4535 gram substance gave 0.0228 gram nitrogen.

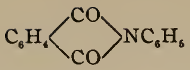
	Calculated for $C_{15}H_{11}O_2N$.	Found. I.	 II.	 III.
N	5.90	5.34	5.57	5.03

On keeping it in a fused condition for three hours it was found to change to *s*-orthotolylphthalimide with the melting-point 197°. By heating the substance with water in a sealed tube for seven hours, at 120°, it was noticed that a part decomposed to phthalic acid and orthotoluidine and a part changed to *s*-orthotolylphthalimide, but by the action of baryta water it was decomposed almost entirely into orthotoluidine and phthalic acid.

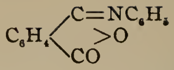
Oxyphthalylnitrosoorthotoluidine, 
$C_6H_4\begin{cases}CON(NO)C_6H_4CH_3\\COOH\end{cases}$.
—Orthotolylphthalamic acid, 
$C_6H_4\begin{cases}CONHC_6H_4CH_3\\COOH\end{cases}$, prepared by boiling *s*-orthotolylphthalamide with concentrated aqueous ammonia, was found to yield a nitroso compound under conditions similar to those of *s*-phenylphthalamic acid by the action of nitrous acid. The behavior of this nitroso compound very much resembles that of the nitroso compound from phenylphthalamic acid in all respects except in its explosiveness, which is not so violent as the former.

Theoretical Views.

Since the existence of two isomeric phthalimides and substituted phthalimides is possible as has been shown in the previous part of the paper, we naturally consider that two isomeric phenylphthalimides are possible, their constitutions being represented by the following formulas:

(*A*)


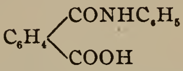
$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NC_6H_5$$

(*B*)


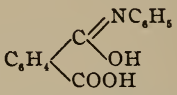
$$C_6H_4\left<\begin{matrix}C{=}NC_6H_5\\ \quad >O\\CO\end{matrix}\right.$$

But, in fact, we have noticed the existence of two isomeric phenylphthalimides formed by the action of aniline upon phthalyl chloride, one melting at 203° and the other at 235°.

By the action of alkali, *s*-phenylphthalimide ought to yield an acid corresponding to the formula *A′* and *a*-phenylphthalimide, an acid corresponding to *B′* :

(*A′*)


$$C_6H_4\left<\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right.$$

(*B′*)


$$C_6H_4\left<\begin{matrix}C\left<\begin{matrix}{=}NC_6H_5\\OH\end{matrix}\right.\\COOH\end{matrix}\right.$$

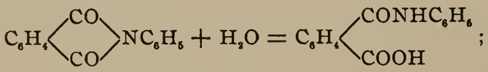
It is highly probable that the acid formed from ordinary phenylphthalimide possesses the structure *A′*, which is in harmony with its formation, transformation, and decomposition :

(1) An acid commonly known as phthalanilic acid (phenylphthalamic acid) is readily formed from ordinary phenylphthalimide by means of baryta water or alcoholic ammonia.

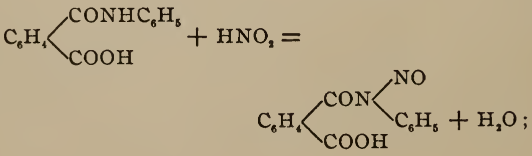
(2) Phenylphthalamic acid yields a nitroso compound by the action of nitrous acid, showing the presence of the imido group.

(3) On boiling the nitroso compound with water, it yields principally phenol and phthalic acid with the evolution of nitrogen, and simultaneously some nitrous acid is evolved with the formation of ordinary phthalimide.

Now, if we admit the correctness of the formula *A* for ordinary phthalimide and *A′* for phthalamic acid, the formation, transformation, and decomposition represented above can readily be interpreted :

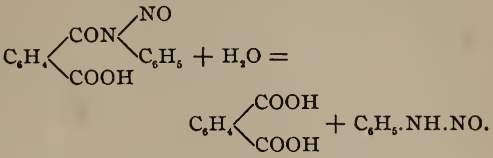
(I)


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NC_6H_5 + H_2O = C_6H_4\left<\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right. ;$$

(II)


$$C_6H_4\left<\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right. + HNO_2 =$$

$$C_6H_4\left<\begin{matrix}CON\left<\begin{matrix}NO\\C_6H_5\end{matrix}\right.\\COOH\end{matrix}\right. + H_2O ;$$

(III) (*a*)


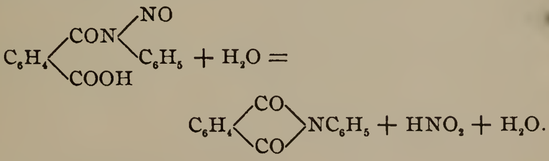
$$C_6H_4\left\langle\begin{array}{l}CON\left\langle\begin{array}{l}NO\\C_6H_5\end{array}\right.\\COOH\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}COOH\\COOH\end{array}\right. + C_6H_5.NH.NO.$$

The compound C_6H_5NHNO, which is a desmotropic form of diazobenzene, may soon change to the latter, and the diazobenzene thus formed being incapable of existence immediately decomposes into phenol and nitrogen by the action of water, thus :

$$(b)\quad C_6H_5.NH.NO \rightarrow C_6H_5.N:N.OH,$$

$$(c)\quad C_6H_5.N:N.OH = C_6H_5.OH + N_2,$$

and the simultaneous formation of nitrous acid and ordinary phenylphthalimide from the nitroso compound may depend upon the following reaction :

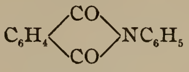
(*d*)


$$C_6H_4\left\langle\begin{array}{l}CON\left\langle\begin{array}{l}NO\\C_6H_5\end{array}\right.\\COOH\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle NC_6H_5 + HNO_2 + H_2O.$$

As the ordinary phenylphthalimide appears thus to possess the symmetrical structure, the new and isomeric phenylphthalimide ought to have the unsymmetrical form as described above. And, there are several facts which lend support to the latter view.

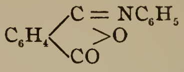
The new phenylphthalimide, when perfectly dried, changes with slight decomposition to ordinary phenylphthalimide when heated in a test-tube, but when heated in a sealed tube at 140°, dissolved in an indifferent solvent such as xylene, it undergoes a similar change almost without decomposition, while ordinary phenylphthalimide sublimes without the slightest change even at high temperature. Consequently, phenylphthalimide appears to exist in two forms, a stable and an unstable form.

As ordinary or stable phenylphthalimide has already been found to have the symmetrical structure, it is highly probable that the new or unstable phthalimide possesses the unsymmetrical structure, as the following formulas show:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5$$

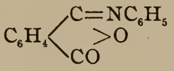
Stable form.
s-Phenylphthalimide.



$$C_6H_4\left\langle\begin{matrix}C = NC_6H_5\\ \quad >O\\ CO\end{matrix}\right.$$

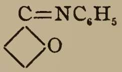
Unstable form.
a-Phenylphthalimide.

On further comparison of the behavior of both phenylphthalimides, that of the new variety points to the unsymmetrical formula as the more probable. On heating ordinary phenylphthalimide with a small quantity of water it undergoes no change at all, while the new phenylphthalimide readily decomposes under this treatment into aniline and phthalic acid, with the simultaneous formation of some ordinary phenylphthalimide. This decomposition of the new phenylphthalimide by water is similar to that of phenyl isocyanate, the latter readily yielding aniline and carbon dioxide under similar conditions. It seems probable, therefore, that the linking of the carbon and nitrogen atoms in both compounds may be alike, as shown in the formulas:



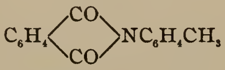
$$C_6H_4\left\langle\begin{matrix}C{=}NC_6H_5\\ \quad >O\\ CO\end{matrix}\right.$$

a-Phenylphthalimide.



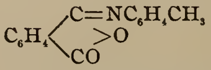
Phenyl isocyanate.

The ordinary and the new orthotolylphthalimides behave exactly like the *s*- and *a*-phenylphthalimides, respectively, as has already been stated. Consequently, ordinary orthotolylphthalimide should possess the symmetrical, and the new one the unsymmetrical structure, as the following formulas show:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_4CH_3$$

s-Orthotolylphthalimide.



$$C_6H_4\left\langle\begin{matrix}C{=}NC_6H_4CH_3\\ \quad >O\\ CO\end{matrix}\right.$$

a-Orthotolylphthalimide.

It may be that phthalyl chloride exists in two different forms according to the temperature. At ordinary temperature it may assume the normal form and at the lower temperature the unsymmetrical form.

IMPERIAL UNIVERSITY,
KYOTO, April 12, 1901.

REPORT.

The Chemistry of the Purine Group.

In previous numbers of this JOURNAL[1] the important contributions to the chemistry of uric acid and its derivatives have been reported. Within the last few years the subject has been very actively investigated, and as a result this chapter of organic chemistry, which has occupied the attention of Liebig and Wöhler and of A. von Baeyer, has been closed through the magnificent researches of Emil Fischer. These investigations, which have extended over nearly twenty years, have recently been summed up by Fischer[2] in a long article. It is from this source that the following brief review is largely taken.

The older investigators had studied uric acid, xanthine, and hypoxanthine, and had put forward formulæ for these substances expressing the facts which had been established by a study of their reactions; but there was no experimental proof of the relations between them. Fischer speaks with some feeling of the tendency of some chemists to advance complicated formulæ on very insufficient grounds, and calls attention to the fact that too much weight is often given to a successful guess, while a mistake is too readily condoned. Formulæ put forward by Medicus, which have been accepted by chemists, stand as correct only as the result of great labor by Fischer and his helpers.

The discovery by Fischer, about eighteen years ago, of the action of phosphorus pentachloride upon a methyl derivative of uric acid, gave a new point from which to attack these compounds. A substance containing chlorine was formed, which could be converted into a number of compounds by various reagents. This substance had the formula

$$CH_3.C_5N_4Cl_3.$$

It was evidently a substitution-product of a compound of the composition $CH_3.C_5N_4H_3$, which in turn could be considered as a methyl derivative of the complex $C_5N_4H_4$. To a compound of this composition, which was apparently the mother-substance of the uric acid group, the name purine (from *purum* and *uricum*) was given. The experimental work had, therefore, a new and definite aim—the preparation of purine and its derivatives, and the proof of their structure.

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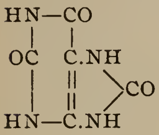
[1] This JOURNAL, 6, 360; also 4, 406 and 12, 138.

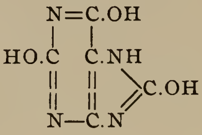
[2] Ber. d. chem. Ges., 32, 435.

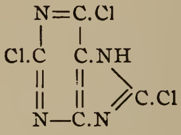
The empirical relations between the simple members of the group are represented as follows:

$C_5N_4H_4$	$C_5N_4H_4O$	$C_5N_4H_4O_2$	$C_5N_4H_4O_3$
Purine.	Hypoxanthine.	Xanthine.	Uric acid.

The structure of uric acid is represented by formula I. below—that of Medicus—or by formula II.

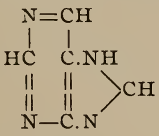

I.

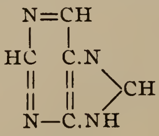

II.


III.

The first is in accord with most of the well established facts; by the use of the second, however, the action of phosphorus pentachloride upon uric acid can be more readily followed. In this action three oxygen and three hydrogen atoms are replaced by three chlorine atoms, and trichlorpurine (formula III.) is formed. The acid contains, therefore, apparently three hydroxyl groups. On account of the fact that it is impossible to distinguish experimentally between the lactam and lactim formulæ, the older formula for uric acid is used. The same kind of tautomerism is observed in the case of the other oxygen derivatives of purine.

Trichlorpurine (formula III.) is converted into purine by replacing the chlorine atoms by hydrogen. The structure of purine is, therefore, represented by formula IV. Methyl derivatives of the tautomeric form (formula V.) have been pre-

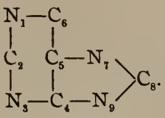

IV.


V.

pared, but only one hydrogen compound has been isolated.

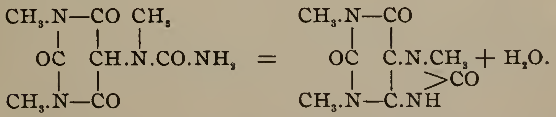
Purine yields mono-, di-, and trioxy, as well as halogen, amino, sulpho, and hydrazo derivatives. From these substances methyl derivatives have been prepared in great number on account of the unusual chances for isomerism.

In order to facilitate naming the compounds the atoms in the purine chain have been numbered in the following manner:



In the preparation of these compounds three general methods have been employed:

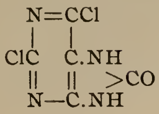
(1) Derivatives of uric acid have been prepared by the condensation of pseudouric acids. This synthesis, which had been used to some extent by the early investigators, was made of great practical value by Fischer by using as dehydrating agent oxalic or hydrochloric acid. Starting with pseudouric acids containing methyl groups in the ring or side chain, a number of isomeric substances have been prepared. In this way hydroxycaffeine was formed from 1,3,7-trimethylpseudouric acid:

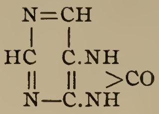


(2) A number of compounds have been prepared by the introduction of alkyl groups into uric acid and other purine derivatives. Fischer improved this method markedly by introducing the groups in the wet way. By working in alkaline solution, many substances were obtained by varying the temperature and the proportions of the reagents. This method furnished the first direct synthesis of caffeine from xanthine.

(3) The preparation of purine derivatives through the chlorpurines is the most important method. These chlorine compounds are prepared by the action of phosphorus oxychloride and pentachloride on the oxygen compounds. By regulating the action of the chlorinating agent the oxygen atoms can be replaced step by step. For example, phosphorus pentachloride at 160° converts the potassium salt of uric acid into 8-oxy-

2,6-dichlorpurine (formula VI.). At a higher temperature


VI.


VII.

three atoms of oxygen are removed by phosphorus oxychloride and trichlorpurine is formed. When 1,3,7-trimethyluric acid is treated in the same way only one chlorine atom is introduced. In some cases phosphorus pentachloride causes the elimination of one or more of the methyl groups; 3,7,9-trimethyluric acid, for instance, is converted by the chloride into 7,9-dimethyl-8-oxy-2,6-dichlorpurine. All of the chlorine compounds can be readily reduced. In this way trioxypurines can be converted into dioxy- and monoxypurines. For example, uric acid (trioxypurine) can be changed into 8-oxy-2,6-dichlorpurine, which, by reduction, becomes a monoxypurine (formulas VI. and VII. above).

Oxyhalogen compounds readily yield to hydriodic acid and phosphonium iodide and give hydrogen derivatives. When no oxygen is present, however, the chlorine substitution-products are completely decomposed by the reducing agents at ordinary temperature; but at 0° they are converted into iodo compounds, which can, in turn, be reduced by means of zinc dust. For example, 7-methyldichlorpurine gives 7-methyliodopurine, which can be converted into 7-methylpurine. If a chlorpurine is treated with zinc dust directly, a part of the halogen is left in the compound. 7-Methyltrichlorpurine is in this way changed into 7-methyl-2-chlorpurine.

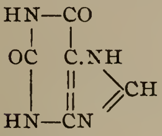
Water, acids, and alkalies react with the chlorpurines and cause a partial or complete conversion of the halogen atoms into hydroxyl groups. Sodium hydroxide, for example, reacts with trichlorpurine at ordinary temperature to form 6-oxydichlorpurine, while at 130°, with hydrochloric acid, uric acid is formed.

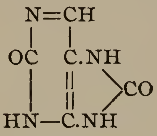
An aqueous solution of potassium hydrosulphide converts chlorpurines into thiopurines. With ammonia, aminopurines are formed, which, with nitrous acid, yield oxy-derivatives.

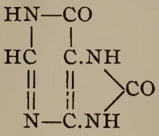
Combinations of the methods briefly outlined above have produced a large number of substances, which exhibit the phenomenon of isomerism in a marked degree. While all the isomers which are possible as a result of the structural formulæ put forward for the simplest members of the purine group have not in every case been prepared, the number definitely established is very large, and each compound has found its place in the system.

Uric acid and its derivatives have been exhaustively studied. It is the only trioxypurine possible. The structure assigned to it calls for a number of methyl derivatives in which the radical is joined to nitrogen. There are 4 monomethyl, 6 dimethyl, 4 trimethyl, and 1 tetramethyl derivatives. The compounds have all been prepared, and the structure has been established in each case.

There are three possible dioxypurines which contain the oxygen linked as in uric acid. Their formulæ are as follows:

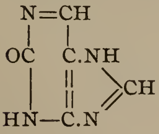

VIII.

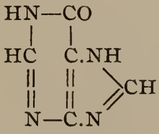

IX.

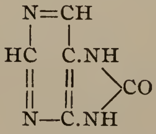

X.

Compounds having the structure of formulæ VIII. and IX. and methyl derivatives of the formula X. are known. 2,6-Dioxypurine, which is xanthine (VIII.), should furnish 3 mono-, 3 di-, and 1 trimethyl derivatives. They have all been prepared. Five methyl derivatives of 6,8-dioxypurine and 2 of 2,8-dioxypurine are also known.

Of the 3 monoxypurines those having formulæ XI. and XII. have been isolated.


XI.


XII.


XIII.

6-Oxypurine (XII.) is the natural product hypoxanthine. It has been prepared synthetically from trichlorpurine. Four of its methyl derivatives and all of those of 8-oxypurine have been described, while but one substance derived from 2-oxypurine is known.

From the above it is seen how complete is the series of oxygen compounds. In addition to these, the purine group contains a large number of amino, thio, and halogen derivatives, as well as substances which contain two or more groups of a different nature. In all 146 purine derivatives have been described, and of this number all but 18 are the result of the work of Fischer and his pupils.

The methods which have been used to determine the structure of the members of this group include both synthesis and the regulated decomposition into simpler known compounds. In many cases both methods have been applied to the same substance with confirmatory results. In order to illustrate the methods, one of the proofs of the structure of 3,7,9-trimethyluric acid will be given.

When uric acid is treated with methyl iodide under certain conditions, a monomethyl derivative is obtained. This compound is readily split into alloxan and methylurea. The methyl group is, accordingly, in the imidazole ring, for uric acids containing a methyl group in the other ring give methyl alloxan. When this methyluric acid is heated with hydrochloric acid it is decomposed into carbon dioxide, ammonia, methylamine, and glycocoll. The formation of the latter substance shows that the methyl group occupied position 9. This 9-methyluric acid is converted by phosphorus pentachloride into a 9-methyloxydichlorpurine. The position of the oxygen and chlorine atoms is immaterial as far as the present line of proof goes. This substance yields a dimethyl compound, which gives sarcosine when heated with hydrochloric acid. As the formation of glycocoll is evidence of the presence of a methyl group in position 9, so the formation of sarcosine indicates that there is a methyl group in position 7. The compound is, therefore, 7,9-dimethyloxydichlorpurine. Water removes the chlorine and a dimethyluric acid results, which must have the substituting groups in positions 7 and 9. This compound yields a trimethyl derivative. As the same substance is obtained by the methylation of 3,7-dimethyluric acid, it is evidently 3,7.9-trimethyluric acid.

A brief account of the synthesis and the determination of the structure of a few important members of the group will further serve to make the methods clear. Xanthine is prepared from uric acid, as follows: The acid is converted, by means of phosphorus pentachloride, into trichlorpurine, which yields, with hydriodic acid, diiodopurine. This compound loses its halogen when heated with hydrochloric acid, and, as a result, xanthine is formed. When the lead salt of xanthine is heated with methyl iodide, two methyl groups are introduced in positions 3 and 7, and theobromine is formed. When methylated in alkaline solution, xanthine gives 1,3,7-trimethylxanthine (caffeine).

Theobromine has been prepared without the intermediate formation of xanthine. Uric acid was converted into its 3-methyl derivative, from which was prepared 3-methylchlorxanthine by means of phosphorus pentachloride. This compound on methylation was converted into 3,7-dimethylchlorxanthine, which was readily reduced to theobromine.

Six independent syntheses of caffeine have been devised. In the one cited above uric acid was the starting-point. In another interesting synthesis dimethylalloxan was converted into 1,3,7-trimethylpseudouric acid, from which xanthine was easily obtained.

The structure of theobromine is proved by effecting its synthesis from 3,7-dimethyluric acid through 3,7-dimethyloxychlorpurine. The structure of caffeine follows from its numerous syntheses, which can be traced, step by step. It is further proved by its decomposition-products. Chlorine in aqueous solution splits it into dimethylalloxan and methylurea. It contains, as a consequence, two methyl groups in the alloxan ring. The third methyl group is shown to occupy position 7 by the formation of sarcosine when caffeine is decomposed by barium hydroxide.

The preparation of purine was effected only toward the end of the work, after a great amount of research. The method of reduction with hydriodic acid and phosphonium iodide, which proved of such great value with a number of chlorpurines, could not be used to convert trichlorpurine into purine. At ordinary temperature the reagents caused the complete decomposition of the compound. It was discovered, finally, that at 0° a partial reduction took place and diiodopurine was formed. The halogen was removed from this substance by zinc dust, and purine was obtained. The compound is a high-melting substance whose great solubility in water is in striking contrast with the small solubility of its derivatives. It is inert toward oxidizing agents and possesses acid and strong basic properties.

The work which has been reviewed is almost entirely that of Fischer. While other chemists have been doing good work in this field of late, they have not added materially to the theoretical side of the subject, and, consequently, their investigations have not received the attention which they would merit in a more extended account of this important chapter of organic chemistry.

JAMES F. NORRIS.

MASS. INST. OF TECHNOLOGY.

SELECT METHODS IN FOOD ANALYSIS. By HENRY LEFFMANN, A.M., M.D. and WILLIAM BEAM, A.M., M.D. pp. 383. Philadelphia: P. Blakiston's Son & Co. 1901. Price $2.50.

The unique value of this book lies in the fact that it gathers together better than has been done anywhere else the methods of food analysis which have appeared in the bulletins of the United States Department of Agriculture and of the Association of Official Agricultural Chemists. Many of these are now out of print and difficult of access and the publication of the more important parts of many of them in a permanent form will prove very useful.

The work is not, of course, confined to material from the source mentioned, but covers the general subject of food analysis in a comprehensive manner. About 70 pages are devoted to general analytical methods, both physical and chemical. Twenty pages are given to the discussion of general methods for the detection of poisonous metals, colors, and preservatives. In the remainder of the book special topics are considered, including starch, flours and meals, sugars, fats and oils, milk and milk products, tea, coffee, cocoa, condiments and spices, alcoholic beverages, meats and meat extracts.

The selection of material is, in general, satisfactory, and as much is included as could be expected of a book of this size. Occasionally there is a tendency to describe complex forms of apparatus which are useful when many determinations of the same kind are to be made, but which are less suitable than simpler forms for the occasional use of most laboratories. For distillation under diminished pressure, for instance, it would be well to give the simple combinations of ordinary apparatus which may be used in any laboratory having water under pressure.

A few slips indicate the haste with which the book has been prepared. Thus, under indicators, the weights of methyl-orange and of cochineal to be taken in preparing solutions are given but not the volume of the solvent. Such errors are not, however, numerous, nor important. W. A. N.

ELEKTROCHEMISCHES PRAKTIKUM. Von RICHARD LORENZ, Dr. phil., ord. Professor am eidg. Polytechnikum in Zurich, Vorstand der Abtheilung für Elektrochemie und physikalische Chemie. Mit 90 Abbildungen im Text. Göttingen: Vandenhoeck und Ruprecht. 1901. pp. 234.

This excellent little book by Lorenz undoubtedly supplies a need in the field of electrochemistry. There are books which have to do with special phases of electrochemistry, as conductivity, or electrolytic separation of the metals, etc., but there is no work available having the same scope as the one in hand. This will be seen by a glance at its contents. The first part of the work deals chiefly with the apparatus used in making electrochemical measurements.

The second part is especially interesting, dealing with the electrolytic preparation of a number of familiar compounds, such as potassium chlorate, perchlorate, persulphate, permanganate, etc. The purification of a number of substances by electrolysis is also taken up.

Analysis by electrolysis, and electrolytic methods applied to copper, silver, zinc, cadmium, iron, antimony, tin, mercury, lead, etc., are treated of at some length. This chapter is very useful at present, since analysis by electrolysis, as is well known, has come into great prominence in the last few years.

The rest of the book has to do mainly with the measurement of electromotive force.

The book is clearly written and well illustrated, and is a valuable addition to the literature of physical chemistry. As a laboratory guide in electrochemistry, it is sure to find its place in every laboratory where electrochemical work is done.

H. C. J.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), C. A. BISCHOFF (Riga), E. F. DÜRRE (Aachen), J. M. EDER (Wien), P. FRIEDLAENDER (Wien), C. HAEUSSERMANN (Stuttgart), F. W. KÜSTER (Clausthal), J. LEWKOWITSCH (London), M. MÄRCKER (Halle), W. MUTHMANN (München), F. RÖHMANN (Breslau), herausgegeben von RICHARD MEYER (Braunschweig). X Jahrgang, 1900. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1901. 555 pp. Price, 14 marks.

Again chemists will experience the pleasure which the editor and publishers of this excellent publication prepare for them annually. Whatever branch of chemistry one may be interested in, this volume will give him a clear, satisfactory résumé of the work done in his special line. The titles of the chapters and the authors are as follows: Physical Chemistry, by F. W. Küster; Inorganic Chemistry, by W. Muthmann; Organic Chemistry, by C. A. Bischoff; Physiological Chemistry, by F. Röhmann; Pharmaceutical Chemistry, by H. Beckurts; Chemistry of Food Stuffs, by H. Beckurts; Agricultural Chemistry, by M. Märcker and by W. Naumann; Metallurgy, by E. F. Dürre and Fr. von Kügelgen; Fuels and Explosives, by C. Haeussermann; Technology of the

Carbohydrates and Brewing, by W. Märcker, W. Naumann, and E. H. Schultze ; Technology of the Fats and Petroleum, by J. Lewkowitsch ; The Chemistry of Tar and Dyes, by Richard Meyer ; Chemical Technology of the Textile Fibers, by P. Friedlaender ; Photography, by J. M. Eder and E. Valenta.

Judging by the previous volumes, this one will prove of great service to all working chemists. It will serve to recall to their minds those investigations which they are already somewhat familiar with through reading of the journals, and will, no doubt, also reveal many interesting articles that are not so familiar. It is a book which should be in every chemical library.

VOL. XXVI. DECEMBER, 1901. No. 6.

AMERICAN

CHEMICAL JOURNAL

A NEW APPARATUS FOR DETERMINING THE RELATIVE VELOCITIES OF IONS; WITH SOME RESULTS FOR SILVER IONS.[1]

BY WILLIAM T. MATHER.

This investigation was undertaken for the purpose of determining the *relative velocities of the ions of a number of silver salts in water, and in methyl and ethyl alcohols.* The work thus far has had to do chiefly with the improvement of the apparatus to be used, the experiments being limited to solutions of silver nitrate in water and in ethyl alcohol, and silver acetate in water.

The Apparatus.

An examination of the results obtained by previous experimenters makes it clear that there must have been serious errors in the methods which they employed. Although all of these methods depend upon the same principle, *i. e.*, the passage of a known amount of current through the solution of the electrolyte, and the subsequent separation and analysis of the solutions around the anode and cathode, yet the velocities as determined differ greatly even in experiments conducted under similar conditions. Previous investigators have relied upon the difference in specific gravity resulting from the electrolysis to secure a separation of the two portions of the solution, the anode and cathode being placed at different levels in the apparatus used. No means were, however, provided for a final division of the liquid at the close of the electrolysis, and the discrepancies in the results are probably to be explained by an incomplete separation of the anode and cathode portions, either during the experiment or at the close when they are drawn off for the purpose of analysis.

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[1] From the Dissertation of the author, submitted to the Board of University Studies of the Johns Hopkins University, for the Degree of Doctor of Philosophy. June, 1897.

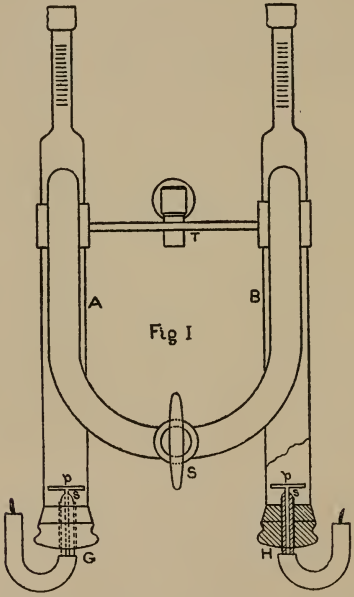
Fig I

It seemed desirable, therefore, at the start to devise a form of apparatus which should be, as far as possible, free from these defects. The objects in view were: First, that it should be symmetrical in form, permitting the passage of the current in either direction; second, that it should contain a sufficient quantity of solution to allow a large change in concentration, and thus permit of greater analytical accuracy; third, and most important, that there should be a means of completely separating the solution at the close of the electrolysis, into two portions of accurately determined amount; fourth, that the possibility of diffusion should be, as far as possible, prevented.

A large number of experiments were made with several pieces of apparatus, and the form here described was decided upon as best fulfilling the desired conditions (Fig. I.). It was made of glass, by Emil Greiner of New York.

The two limbs (A and B) are about 18 cm. long, 2 cm. in diameter, and are then contracted above for an additional length of 6 cm. to a diameter of 0.5 cm., the reduced portions being graduated in millimeters. These limbs are connected near the upper ends of the larger portions by a U-tube about 0.5 cm. in diameter, the bottom of which is some 2 cm. above the level of the lower ends of the limbs. At the center of the tube is a stop-cock (S) of large bore. The lower ends of the limbs are closed by glass stoppers (G and H), through which holes were bored for the insertion of the electrodes. These latter were made of pure silver prepared by reduction of washed silver chloride, which in turn was precipitated from the nitric acid solution of pure mint-silver. Each consists of a round plate (*p*), autogenically welded to a silver stem (*s*), which is firmly secured in the glass stopper by means of a piece of pure gum tubing, which was placed in the hole in the stopper and the stem forced through it. To the outer end of the stem was soldered a flexible conductor which was covered by pure rubber tubing to prevent leakage of the electric current, when the apparatus is placed in the thermostat. In order to permit of leveling the apparatus and also of securing it in the bath, the apparatus was cemented into a brass frame, which, by means of a tube and clamp screw can be secured to an upright rod upon the table or in the bath.

For the determination of the effect of temperature, a form of bath was constructed by the writer which proved extremely efficient, remaining constant to 0°.1 for long periods of time. It consists (Fig. II.) of a double-walled copper vessel with concave bottom, the space between the walls being filled, by means of a stop-cock and cup (C), with a mixture of glycerin and water,

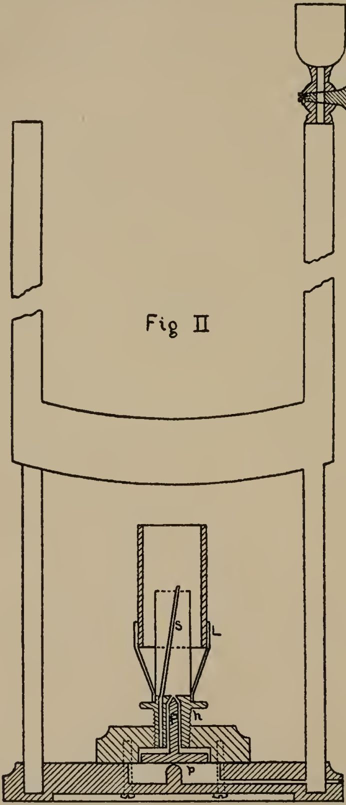
Fig II

which was employed both because of its large expansion coefficient and because of its preservative action upon the rubber diaphragm. From this annular space communication is made with a space below the diaphragm beneath the bunsen burner (L). Resting upon this diaphragm is a small conical peg (P), which, by motion of the diaphragm through expansion of the liquid, controls the supply of gas which enters through a side tube (not shown) above the diaphragm. A minute constant flame is supplied by a small tube (S) extending from the gas chamber above the diaphragm to the top of the burner tube. The burner itself can be raised from the peg (P) by means of a threaded connection (*h*) with the gas chamber, and by means of this adjustment and the stop-cock and cup before mentioned, any desired temperature above that of the room can be easily obtained. The arrangements of the diaphragm and burner are due to Professor Henry Carmichael, of Boston. It is, however, perfectly feasible to use the vessel in connection with a thermo-regulator of the type designed by Professor Ostwald, the annular space taking the place of the glass bulb commonly employed. The advantages secured by this arrangement are that the expanding liquid is alone subject to any marked change of temperature, and the water of the bath being thus protected is maintained at a practically constant temperature without recourse to a stirrer.

For determinations at 0° the apparatus was placed in a copper tank filled with finely broken ice, the tank being jacketed with a thick layer of powdered cork and a wooden case.

The electric current, which was supplied by a battery of 40 storage cells, was measured by means of two silver voltameters consisting of platinum crucibles and pure silver anodes, the supports for the crucibles and all electric connections being insulated with vulcanite and mica. The crucibles were heated, cooled in a desiccator, and weighed before each experiment, and the deposit formed by the current was treated in accordance with the directions given by the Committee of the National Academy of Sciences. During the early stages of the investigation the attempt was made to avoid the use of voltameters by employing a form of d'Arsonval galvanometer, designed by Professor Rowland, the same being calibrated by means of a voltameter. In order to secure constancy, in spite of the varying temperature of the room, all the resistances used in the main circuit and galvanometer shunt were placed in a constant-temperature oil-bath, of the same construction as the one already described. It was found, however, after a number of experiments had been made, that, possibly owing to changes in the suspension filament or to the effects of temperature variations, sufficiently accurate results could not be secured, and further use of the same was abandoned, save as a control, readings being taken every few hours.

Preparation of Solutions.

The analyses were made by titration with ammonium sulphocyanate solutions, ferric ammonium sulphate being used as an indicator. Special care was taken in the preparation of the solutions, and by frequent comparisons with freshly prepared standards of potassium chloride, their strength was accurately determined, the error being not more than 0.02 cc. in 90 cc., or less than 1 part in 4,000. In the preparation of the potassium chloride standards small amounts of the salt were taken, dried in an air-bath in weighing tubes at 140° C., cooled in a desiccator, and weighed. These were then dissolved in water and titrated against silver nitrate. The salt used was purified by repeated crystallization by Dr. H. C. Jones, who also kindly prepared the silver acetate. The ferric ammonium sulphate was made under the direction of Dr. Renouf, while the silver nitrate was in part made from pure silver, prepared as described before, and in part from the commercial article, freedom from acid being secured by repeated recrystallizations. The water used in the preparation of the solutions and for the washing out of the apparatus was obtained by redistillation of ordinary distilled water, to which a solution of chromic acid had been added, the steam passing through a strong boiling alkaline solution of potassium permanganate. The apparatus was arranged according to the plan described by Jones and Mackay.[1] The absolute alcohol was prepared by distillation from lime and subsequent further dehydration with copper sulphate, and the dilute solutions were made from this, their exact strengths being determined with an alcoholometer.

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[1] Ztschr. phys. Chem., **22**, 237.

In the preparations of the solutions in absolute alcohol and also in filling the apparatus with the same, special care had to be taken in order to prevent the absorption of moisture, since pure alcohol is an extremely deliquescent substance. The method adopted was as follows: The silver nitrate being placed in a dry liter flask, the latter was filled by means of a siphon from the bottle containing the alcohol dehydrated over copper sulphate, an intermediate filter being introduced to prevent the passage of any particles of the sulphate which the alcohol might contain in suspension. The top of the funnel was closed by a glass cap, the joint between being carefully ground, and the flow of the liquid was started by aspiration through the drying tube, which was connected through a hole in the cap. For this drying tube, as well as those which permitted the entrance of air to the bottle and flask, long U-tubes filled with dehydrated copper sulphate and glass wool were used. The resulting solution of silver nitrate was removed from the flask to a dry bottle in a similar manner, the intermediate filter, however, not being employed. This bottle was permanently closed by a rubber stopper (which had been previously boiled in silver nitrate), connection with the interior being made by a glass tube and drying tube, the openings being capped with rubber tubes and glass plugs. When it was desired to fill the burette for the purpose of analysis or to fill the apparatus, these plugs were removed and the point of the burette inserted into the tube, the rubber tube making a tight joint. The solution was then drawn up into the burette by aspiration through the drying tube, which closed its upper end. In filling the apparatus, the end of the burette was similarly inserted into one limb of the apparatus, the other limb being closed with a drying tube. After filling, both limbs were connected by means of rubber tubes with a series of drying tubes, in order to allow of equality of pressure inside and outside of the apparatus.

The flasks and burettes used were calibrated by means of the apparatus designed by Morse and Blalock,[1] calibration being repeated at least twice.

Method of Analysis.

In the analysis of the solutions after electrolysis it was noticed that if, after the first faint change of color was secured, the solution was allowed to stand for some time, the color grew gradually much darker, and if a known amount of silver nitrate solution of strength equal to the sulphocyanate was then added and the titration again completed, less than the same amount of the sulphocyanate solution was required to cause a return of the color. It was generally necessary to repeat this process several times before a constant state was reached. If, however, when this had been obtained, the solution was allowed to stand, the first tinge of color remained constant for several hours, but finally faded out. The following results of one analysis will render this clear:

$AgNO_3$ N/10. Cubic centimeters.	NH_4CNS N/10. Cubic centimeters.	Corrected amount of NH_4CNS N/10. Cubic centimeters.
0	94.89	94.89
0.23	95.06	94.83
0.51	95.30	94.79
0.74	95.50	94.76
1.17	95.89	94.72
1.83	96.55	94.72
2.18	96.90	94.72

It was noticed that the precipitate first formed was very flocculent, even with the most rapid stirring, but gradually, if the titration were repeated as above, it became granular and settled quickly. We may possibly explain the above results by supposing, as has been found in other cases, that some of the sulphocyanate was occluded in the precipitate first formed.

The sharpness of the color change was increased by the use of a stirrer formed of a bent glass rod which, by means of a flexible shaft and suitable connection, was rapidly rotated by an electric motor.

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[1] This JOURNAL, 16, 479 (1894).

The analysis of the alcoholic solutions at first presented some difficulty, as no data could be found as to the effect of alcohol upon the accuracy of the Volhard method. A series of comparisons was, therefore, made of N/10 solutions of silver nitrate and sulphocyanate, different amounts of alcohol being added. In concentrated alcoholic solutions it was found impossible to secure good results, the nitric acid reacting upon the alcohol and causing the formation of polymeric aldehydes ("aldehyde-gums"), the brownish color of which prevented the determination of the point of color change of the indicator. Success was, however, secured when the alcoholic solution was diluted to about ten times its original volume before addition of the acid, the latter being added slowly with rapid stirring of the solution. The following determinations will render this evident: The figures give in cubic centimeters the amount of silver nitrate taken, the amount of alcohol, water, indicator, and acid added, and the amount of ammonium sulphocyanate (N/10) necessary to cause a faint permanent change in color.

	$AgNO_3$.	C_2H_5OH.	H_2O.	$FeNH_4(SO_4)_2$.	HNO_3.	NH_4CNS N/10.
I.	48.465	50	500	10	20	48.455

Hence 1000 cc. $AgNO_3$ = 999.8 cc. NH_4CNS N/10.

II.	26.365	20	200	10	20	26.355

Hence 1000 cc. $AgNO_3$ = 999.6 cc. NH_4CNS N/10.

The following three comparisons of a solution of silver nitrate in absolute alcohol with the N/10 solution of sulphocyanate, which were made at different times, further illustrate the accuracy of the method:

	$AgNO_3$.	H_2O.	$FeNH_4(SO_4)_2$.	HNO_3.	NH_4CNS N/10.
I.	45.520	500	10	15	46.025

Hence 1000 cc. $AgNO_3$ = 1082.3 cc. NH_4CNS N/10.

II.	41.30	500	10	20	44.68

Hence 1000 cc. $AgNO_3$ = 1081.9 cc. NH_4CNS N/10.

III.	42.845	500	10	20	46.330

Hence 1000 cc. $AgNO_3$ = 1081.4 cc. NH_4CNS N/10.

Calibration of Apparatus.

For the purpose of calibration the apparatus was clamped to an upright rod permanently secured to the table, and then filled with mercury, the electrodes being protected by a thin coating of shellac, and all air bubbles carefully removed. The central stop-cock was then turned and the separate portions poured out and weighed, the contents of the stop-cock being included with one-half. In this manner the capacity of each limb was accurately determined. Three separate calibrations were made of each of the two pieces of apparatus employed, at the beginning, middle, and close of the time during which the experiments were made, the results of which are given below. The corrections made are calculated from the losses in silver on the electrodes, due to the action of the current, as given by the deposits in the silver voltameter for the different experiments during the time between the calibration in question and the final one.

Apparatus I.

Calibration I., Oct. 20, 1896 :	Per cent.	Corrections.	Corrected per cent.
Right side and stop-cock contains	47.381	+0.025	47.406
Left " "	52.619	—0.025	52.594
Calibration II., Dec. 29, 1896 :			
Right side and stop-cock contains	47.392	+0.012	47.404
Left " "	52.608	—0.012	52.596
Calibration III., Mar. 30, 1897 :			
Right side and stop-cock contains	47.408		47.408
Left " "	52.592		52.592

Apparatus II.

	Per cent.	Corrections.	Corrected per cent.
Calibration I., Oct. 20, 1896 :			
Right side and stop-cock contains	51.257	—0.001	51.256
Left " "	48.743	+0.001	48.744
Calibration II., Dec. 29, 1896 :			
Right side and stop-cock contains	51.260	—0.006	51.254
Left " "	48.740	+0.006	48.746
Calibration III., Mar. 30, 1897 :			
Right side and stop-cock contains	51.253		51.253
Left " "	48.747		48.747

Detailed Description of an Experiment.

The apparatus being fastened to a fixed rod was filled from a burette with the given solution to a mark about half way up the smaller graduated portion of the limbs, and the exact position noted. The reading of the burette and the temperature of the room were also taken. The open ends of the limbs were then closed by stoppers having capillary openings to prevent any increase or decrease of internal pressure due to heating or cooling in the baths, and the whole was secured in the bath (by means of a vertical rod as before) at such a height that the level of the liquid inside and the water outside were practically the same. Connections with the battery and voltameter being made, the electrolysis was allowed to proceed for several hours, the time being regulated according to the strength of the current, as indicated by the galvanometer deflections, these latter also affording a test of the constancy of the current. At the close of the electrolysis a little wax was placed over the capillary openings to prevent any disturbance of the level of the liquid, and the apparatus removed from the bath and clamped to the fixed rod. The wax now being removed, the level of the liquid in the two limbs was brought to equal numbers above or below the fixed marks on the graduated limbs, and the central stop-cock turned. After the whole had acquired the temperature of the room the height of the liquid in the limbs was again noticed, any error due to leakage through the stop-cock or stoppers being thus at once detected. The contents were then carefully washed out, filtered through washed asbestos to remove any disintegrated silver, and analyzed. The amount of silver as found by the analysis was compared with that calculated from the amount of solution placed in the apparatus at the beginning of the experiment, and the accuracy of the result was thus determined. The calculation of the velocity of the ions was then very simple. Thus, in one experiment the apparatus contained at the start 92.965 cc. of N/10 solution of silver nitrate, 48.747 per cent of which = 45.318 cc. was in the left side. The analysis at the close showed a total of 92.968, an amount equivalent to 52.784 cc. being from the left side. The gain at the anode, 7.464 cc., is equivalent to 80.357 mg. of silver. The deposit in the silver voltameter was 152.42 mg., and the velocity of the anion NO_3 is therefore $\frac{80.357}{152.42} = 0.527$. The time of the electrolysis was six hours, and the current, therefore, was equivalent to 0.00631+ amperes.

MEASUREMENTS OF THE VELOCITIES.

Silver Nitrate in Water.

At the beginning of the investigation several experiments were made in which the electrolysis was allowed to proceed for only a short time, and the results showed a higher velocity of the anion than was obtained when the electrolysis was maintained for a longer period. A large number of tests were then made and similar results were obtained, though these differed quite widely among themselves. Though the change in concentration caused by the current was small and the analytical errors therefore large, they were not sufficient to account for the differences found. It was, therefore, apparent, that the cause was to be sought in the apparatus used. The form then employed was a modification of that finally adopted, the limbs being of full size throughout the entire length and the stoppers being at the top. The electrodes were at the ends of glass tubes, which were inserted through the stoppers and extended to the bottom of the limbs, and in order to secure the adjustment of the level of the liquid in the two limbs it was necessary, at the close of the experiment, to slightly raise the stoppers in order to permit the entrance of the air. The experiments being repeated with the later form of apparatus, no difference in the results was obtained within the limits of the experimental errors. The cause of the discrepancy is probably due to the fact that in the first form of apparatus it was impossible to secure an accurate adjustment of level in the two limbs, at the close of the electrolysis, an error being thus introduced, which, though small, was sufficient to account for the differences noted.

In the following tables *t* denotes the temperature of the bath; m the concentration of the solution in gram-equivalents per liter; c the change in concentration expressed in milligrams; v the amount of silver in milligrams, deposited in the voltameter; a the velocity of the anion; while I and II designate the apparatus employed; A and B the voltameters; and L and R indicate whether the anode was in the left or right side of the apparatus.

	t.	m.	c.	v.	a.	
1	0°	0.1	71.486	132.02	0.5414	I, B, R.
2	0°	0.1	66.200	122.43	0.5407	I, A, L.
3	0°	0.1	43.182	79.77	0.5413	II, B, R.
4	47°.9	0.1	80.358	152.42	0.5272	II, A, L.
5	47°.4	0.1	91.425	172.94	0.5286	II, A. R.
6	47°.7	0.1	82.231	155.74	0.5280	I, B, R.
7	29°.1	0.1	27.647	52.04	0.5317	I, A, R.
8	0°	0.025	39.522	73.47	0.5377	I, A, R.
9	45°	0.025	41.955	79.97	0.5246	II, B, L.

The values obtained by other observers under similar conditions are given in the following table:

	Hittorf.			Nernst and Loeb.	
t.	m.	a.	t.	m.	a.
19°	0.118	0.526	20°	0.1043	0.528
19°	0.055	0.526	26°	0.0521	0.524
19°	0.024	0.526	26°	0.025	0.522
			0°	0.025	0.538
			26°	0.0105	0.523

Silver Acetate in Water.

In this investigation it was found impossible to secure exact results in concentrated solutions. The analyses showed not only great variations but also that a considerable loss in silver had taken place. A light-brown deposit of silver oxide was formed on both electrodes, though less upon the cathode, due probably to the formation of complex ions. As was noticed by Nernst and Loeb, if the concentration at the anode became considerable the salt crystallized out; but in most cases this did not interfere with the results.

	t.	m.	c.	v.	a.	
1	0°	0.025	9.99	26.56	0.3746	II, B, L.
2	0°	0.025	23.386	62.82	0.3723	I, A. L.
3	28°.3	0.025	10.84	28.42	0.3818	I, B, R.
4	45°.4	0.025	30.261	79.55	0.389	I, A, R.
5	44°.7	0.025	29.316	75.24	0.3896	II, B, R.
6	49°.4	0.025	28.969	74.79	0.3873	I, A, R.

The average values as given by these results are

t.	*m.*	*a.*
0°	0.025	0.373
28°.3	0.025	0.382
46°.5	0.025	0.389

The value obtained by Nernst, though at greater dilution, is

t.	*m.*	*a.*
24°.5	0.00972	0.376

while that calculated from the above results for the same temperature is

t.	*m.*	*a.*
24°.5	0.025	0.380+

Silver Nitrate in Alcohol.

In these experiments it was found impossible to make use of the ice- or water-bath, as a rapid diffusion of water took place through the stoppers in spite of every precaution. The experiments were made, therefore, at the temperature of the room, the apparatus being placed in a wooden case having a thick cork lining to prevent, as far as possible, any diffusion that might be caused by air currents. The following results were obtained :

Silver Nitrate in Absolute Alcohol.

	t.	*m.*	*c.*	*v.*	*a.*	
1	19°.5	0.10805	32.518	54.85	0.5928	II, B, L.
2	20°.9	0.10805	30.772	51.93	0.5926	I, A, L.
3	20°	0.10805	23.192	38.94	0.5956	II, B, L.

The average of these values is

t.	*m.*	*a.*
20°	0.10805	0.594

Silver Nitrate in 49.7 Alcohol.

	t.	*m.*	*c.*	*v.*	*a.*	
1	24°.4	0.1	79.626	149.8	0.5316	II, B, L.
2	23°	0.1	79.894	149.9	0.5329	II, A, R.

The average of the values is

t.	*m.*	*a.*
23°.7	0.1	0.5323

While in water the velocity calculated for the same temperature and concentration is

t.	*m.*	*a.*
24°	0.1	0.533

It is evident, therefore, that in solutions of this strength the alcohol exerts little or no influence upon the velocity, while in the pure solvent the velocity of the anion $\overline{NO_3}$ is very markedly increased, that of the cation $\overset{+}{Ag}$ being similarly decreased.

Ionic Velocities and Conductivity.

The investigations of Kohlrausch[1] and Ostwald[2] have demonstrated that the molecular conductivity[3] of an electrolyte increases with the dilution and reaches at a definite limit a maximum value; and where the conductivities have been determined through a sufficient range of dilutions it is possible to calculate this value by extrapolation. Kohlrausch also proved by a comparison of the values obtained by him in a large number of salts, with the relative velocities of the ions as given by Hittorf, that μ_∞ is equivalent to the sum of the two independent constants, which are, in fact, the velocities of the ions at infinite dilutions in terms of conductivity units. Denoting these velocities by A and C we have the equation $\mu_\infty = A + C$. Moreover, the calculation of A and C is simple since $C/A = c/a$; where in the case of potassium chloride (KCl), at 25° $\mu_\infty = 140 = A + C$; and since $c = 0.481$ and $a = 0.509$, $\frac{C}{A} = \frac{0.491}{0.509}$, hence $C = 68.6$ and $A = 71.4$. Moreover, experiment shows that the same law holds good for greater concentrations, being, in all, save in the most extreme concentration, equal to the sum of the velocities.

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[1] F. Kohlrausch: Wied. Ann., **26**, 194 (1895).

[2] Ostwald: Lehrb. allg. Chemie, II, 621.

[3] By molecular conductivity is meant the ratio of the conductivity, k, to the concentration in gram-molecules per liter, *i. e.*, $\mu_v = k/m$.

The following table gives the values of the velocities calculated in this manner from the results of the foregoing experiments upon solutions of silver nitrate in water. The conductivities were calculated from those given by Kohlrausch, assuming that the temperature coefficients for different dilutions, as determined between 18° and 25°, hold good between 0° and 48°. t denotes the temperature, m the concentration in gram-molecules per liter, μ_v the conductivity in mercury units, A the velocity of the anion, and C that of the cation. The values of the relative velocities for 18° and 25° were calculated from those obtained at the other temperatures.

t.	m.	μ_v.	A.	C.
0°	0.1	641	347	294
18°	0.1	887	475	412
25°	0.1	1018	542	476
29°.1	0.1	1061	564	497
47°.7	0.1	1448	764	684
0°	0.025	732	394	338
18°	0.025	979	521	458
25°	0.025	1128	598	530
45°	0.025	1617	848	769

The values obtained by Nernst, under similar conditions, are as follows :

t.	m.	μ_v.	A.	C.
25°	0.1	1018	540	478
0°	0.025	732	394	338
25°	0.025	1128	591	537

For solutions of silver acetate in water and for solutions of silver nitrate in alcohol, it is impossible to make exact calculations, as the conductivities have not been determined for concentrations greater than $m = 0.007$ in the case of the acetate, and $m = 0.025$ in the case of the nitrate.

The absolute velocities were calculated in the usual manner from the formulas of Hittorf and Kohlrausch. The following results were obtained, C' being the absolute velocity of the cation and A' that of the anion.

Silver Nitrate in Water.

t.	*m.*	A'_{NO_3}.	C'_{Ag}.
		Cm. per sec.	Cm. per sec.
0°	0.1	0.000382	0.000324
18°	0.1	0.000522	0.000455
25°	0.1	0.000597	0.000524
29°.1	0.1	0.000621	0.000548
45°	0.1	0.000842	0.000753
0°	0.025	0.000434	0.000372
18°	0.025	0.000574	0.000505
25°	0.025	0.000659	0.000584
45°	0.025	0.000934	0.000848

The values obtained by Nernst and Loeb are as follows:

t.	*m.*	A'_{NO_3}.	C'_{Ag}.
		Cm. per sec.	Cm. per sec.
25°	0.1	0.000595	0.000527
0°	0.025	0.000434	0.000373
25°	0.025	0.000651	0.000592

showing a very close agreement with those given above.

It is interesting to compare the result deduced for the cation C' at 18° and $m = 0.1$ with that obtained by W. Whetham,[1] who measured directly the velocities in centimeters by observing the movement of the precipitate formed at the boundary between solutions of silver nitrate and sodium nitrate, the latter containing just enough sodium chloride to make the precipitate visible. He found:

t.	*m.*	C'_{Ag}.
18°	0.1	0.000488 cm. per sec.

The difference between this and that already given, 0.000455, is within the range of experimental errors.

Conclusions.

From the experiments here described we may conclude:

1. That the wide differences observed between the velocities at 0° become less as the temperature rises, the velocities tending towards equality, as has been observed by others.

2. That the effect of decrease in concentration is in the same direction as that of increase in temperature.

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[1] Phil. Trans., (1895), Vol. 186A.

3. That the velocities are largely dependent upon the nature of the solvent.

In conclusion, I wish to express my indebtedness to the late Professor Rowland and to Professor Ames for advice during the progress of this work; to Professor Morse for suggestions in regard to themethod of analysis; and to Dr. H. C. Jones, at whose suggestion this investigation was undertaken, for the preparation and purification of several of the compounds used, and for advice and assistance during the progress of the experiments.

JOHNS HOPKINS UNIVERSITY,
June, 1897.

Supplementary Note.

The work described in the above paper was finished in June, 1897, and a brief account of it was published in the Johns Hopkins University Circular, Vol. 16, No. 130, p. 45, June, 1897. Since that time a number of papers[1] have appeared bearing upon this problem. Of these investigations, by far the most extensive is that of Bein. Indeed, this is the most elaborate investigation on the direct measurement of the relative velocity of ions that has been carried out since the time of Hittorf. Bein describes in all five forms of apparatus with various means of separating the cathode solution from the anode solution. In one of these the two solutions are separated by means of a pinch-cock. In another, the solutions are drawn off in a manner similar to that employed in the apparatus of Nernst and Loeb. In still another form the separation is effected by changing the mercury level, and so on.

On examining the apparatus devised and used by Bein, one is impressed by its comparative complexity. Indeed, three out of the five forms which he constructed are very complex. The question arises whether such a high degree of complexity is necessary in an apparatus for effecting electrolysis and the subsequent separation of the solutions.

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[1] K. Hopfgartner: Ztschr. phys. Chem., **25**, 115; G. Kummel: Wied. Ann., **64**, 655; V. Gordon: Ztschr. phys. Chem., **23**, 469; W. Bein: *Ibid.*, **27**, 1, **28**, 439; O. Masson: *Ibid.*, **29**, 501, Phil. Trans., **192**, A, 331; F. Kohlrausch: Wied. Ann., **66**, 785; A. A. Noyes: Ztschr. phys. Chem., **36**, 61: B. D. Steele: J. Chem. Soc., **69**, 414.

The following results were obtained by Bein for silver nitrate and silver acetate. The velocities given are those of the anion in each case:

$AgNO_3$.	
Velocity of $\overline{NO_3}$.	
At 74°	0.518
" 79°	0.516
" 94°	0.507
" 96°	0.518

CH_3COOAg.	
Velocity of $\overline{CH_3COO}$.	
At 24°	0.413
" 24°	0.414
" 49°.5	0.412
" 96°.5	0.435
" 96°.0	0.442

These results differ considerably from those found by me. The velocity of $\overline{NO_3}$ is smaller, but the temperatures used were higher. This is what we should expect, since it is well known that increase in temperature diminishes the relative velocity of the swifter ion. The above values for $\overline{CH_3COO}$ are higher than those found by me, and the temperatures are higher. This is again what should be expected, since rise in temperature increases the relative velocity of the slower ions.

Kummel and Masson have each devised new forms of apparatus for studying the velocities of ions. These resemble in principle the forms which had already been used.

Quite recently Noyes has described an apparatus which differs considerably from any form previously used. It consists essentially of two U-tubes attached by rubber tubing. The electrodes are inserted into the long arms of the tubes, which are filled with the solution to only a few centimeters above the bend. After the electrolysis was ended, the solution was separated into three portions by inserting a pipette attached to a suction pump.

Steele's method, in general, resembles Masson's, but differs from it in that the measurements are made in water and not in gelatin, and the use of a colored ion as indicator is not necessary.

JUNE, 1901.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXXIII.--THE CONDENSATION OF CARBON TETRACHLORIDE WITH HALOGEN DERIVATIVES OF BENZENE BY MEANS OF THE FRIEDEL AND CRAFTS REACTION.

By James F. Norris and Erik H. Green.

It has been shown[1] recently that the action of carbon tetrachloride on benzene in the presence of aluminium chloride results in a nearly quantitative yield of triphenylchlormethane. As the reaction is a very smooth one, we have studied the condensation of carbon tetrachloride with a number of benzene derivatives, expecting in this way to obtain the corresponding derivatives of triphenylmethane. Among the compounds investigated were certain halogen derivatives of benzene. The behavior of these compounds in the condensation was unexpected; and as the results are of some interest in connection with the application of the Friedel and Crafts reaction to aryl halides, they are given here in the form of a preliminary paper.

Chlorbenzene reacts readily at room temperature with carbon tetrachloride in the presence of aluminium chloride. The product of the reaction was not the expected triphenylmethane derivative, but proved to be an oil, which distilled under diminished pressure without decomposition, and when heated with water lost 2 atoms of chlorine and was converted into 4,4′-dichlorbenzophenone. The yield was good, and the only by-product was a low-melting substance, probably an isomer, which was formed in small quantity. In the condensation but two of the chlorine atoms in the carbon tetrachloride entered into the reaction, and, as a result, a ketone chloride was formed. With benzene, on the other hand, and according to

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[1] Gomberg: J. Am. Chem. Soc., 22, 752; Norris and Saunders: This Journal, 25, 54.

Gomberg and Voedisch,[1] with toluene also, the reaction consists in the removal of three chlorine atoms.

The condensation with brombenzene is analogous to that with chlorbenzene and furnishes a ready means of obtaining a good yield of 4,4′-dibrombenzophenone chloride. This chloride yields the corresponding ketone, when heated with dilute alcohol, which is identical with the compound obtained by Hoffmann[2] from *p*-brombenzoyl chloride and brombenzene. 4,4′-Dibrombenzophenone chloride could not be distilled even under diminished pressure.

The preparation of symmetrical halogen-substituted ketones from carbon tetrachloride seems to be more efficient than the process of condensing substituted benzoyl chlorides with halogen derivatives of benzene. The latter method, according to Schöpff,[3] gives poor yields, and the high temperature at which the reaction is carried out occasions deep-seated changes through the action of the aluminium chloride present. Schöpff heated a mixture of *p*-brombenzoyl chloride and brombenzene with aluminium chloride to 120° to 130° and obtained a small yield of 4,4′-dibrombenzophenone, together with some monobrombenzophenone. The work of Hoffmann[4] also shows that the preparation of di-iodobenzophenone by this process is complicated by the formation of some iodobenzophenone. That these complications are due to the destructive action of aluminium chloride at slightly elevated temperatures is shown by the work of Dumreicher,[5] who found brombenzene and aluminium chloride to react under these conditions to form benzene and dibrombenzene along with ill-defined products.

With carbon tetrachloride, however, the condensation of monohalogen derivatives of benzene proceeds at room temperature, without the formation of resinous by-products. Preliminary experiments show that the alphyl carbon atom, as is general in the Friedel and Crafts reaction, takes the position para to the halogen in the benzene ring.

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[1] J. Am. Chem. Soc., **23**, 177.

[2] Ann. Chem. (Liebig), **264**, 163.

[3] Ber. d. chem. Ges., **24**, 3766.

[4] *Loc. cit.*

[5] Ber. d. chem. Ges., **15**, 33.

The application of the reaction to benzene derivatives containing two halogen atoms was studied carefully, as the preliminary results proved to be at variance with the observations of previous workers who have attempted to condense such compounds by means of aluminium chloride. Heretofore the results have always been abnormal. Methyl chloride, according to Leroy,[1] does not condense with *p*-dibrombenzene, and its unusual action with *o*-dichlorbenzene has been fully described by Friedel and Crafts.[2] The work of Gattermann and Römer[3] on the substituted thiophenes has shown that while the monosubstituted derivatives react normally with acetyl chloride, the dihalogen compounds are either inert or else give rise to a number of complicated compounds, which would not be expected as the result of the reaction. The same observers tried, in vain, to condense acetyl chloride with *p*-dibrombenzene, and Schweitzer[4] was equally unsuccessful with diiodobenzene and with 1,4-dibromnaphthalene. In fact, it has been taken as a rule that the Friedel and Crafts reaction is not applicable to dihalogen compounds.

We have found, however, that when carbon tetrachloride is used as the fatty halide, a condensation takes place normally between it and dichlorbenzene. When a solution of these compounds in carbon bisulphide is treated with aluminium chloride and is heated gently, reaction takes place. The aluminium compound which separates yields, after decomposition with water, a compound which is obtained quite pure after a single crystallization. This substance proved to be the chloride of symmetrical 2,5,2′,5′-tetrachlorbenzophenone. When boiled with dilute alcohol it lost 2 atoms of chlorine and was converted into the corresponding tetrachlorbenzophenone. The structure of the compound follows from its formation from *p*-dichlorbenzene, for in this case there is no opportunity for isomerism.

The easy formation of this tetrachlorketone chloride is the

[1] Bull. Soc. Chim., 48, 214.

[2] Ann. chim. phys., (6), **10**, 411.

[3] Ber. d. chem. Ges., **19**, 691.

[4] *Ibid.*, **24**, 552.

more interesting on account of the fact that Schöpff[1] has shown that the halogen derivatives of the benzene hydrocarbons react with acyl chlorides only when the position para to the aryl halogen is unoccupied. He found, for example, that *p*-bromtoluene does not react with acetyl chloride, while *o*-bromtoluene reacts readily. Our experiments show that when carbon tetrachloride is used the Friedel and Crafts reaction proceeds normally not only when the position para to the aryl halogen is filled, but even when the only position which the alphyl carbon atom can enter is ortho to a halogen in the benzene ring.

Paradibrombenzene reacts with carbon tetrachloride and aluminium chloride. The compound which is formed is now under investigation. Symmetrical tribrombenzene does not react under the same conditions. After heating the reaction-mixture for twenty-five hours all of the tribrombenzene was recovered. Symmetrical tetrabrombenzene behaved similarly. In order to learn whether the stability of these two compounds is due to the accumulation of halogen atoms about the benzene ring, or to the fact that the entering carbon atom must take a position ortho to two halogen atoms, the behavior of unsymmetrical tribrombenzene will be investigated.

Preliminary experiments on the action of carbon tetrachloride in the presence of aluminium chloride on anisol, mesitylene, dimethylaniline, and naphthalene show that these substances readily react at ordinary temperatures. The products will be further studied.

EXPERIMENTAL.

4,4′,-*Dichlorbenzophenone Chloride*.—In the first experiments one molecular quantity of carbon tetrachloride and three and one-half of chlorbenzene were used. As but 2 molecules of chlorbenzene were found to enter into the reaction the proportions of the reaction-mixture were accordingly changed. The same product was obtained when the reaction was allowed to proceed at room temperature and when the mixture was heated to the boiling-point of carbon disulphide.

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[1] *Loc. cit.*, p. 3769.

The preparation was carried out as follows: 20 grams of carbon tetrachloride and 28 grams of chlorbenzene were dissolved in 150 cc. carbon disulphide. To this mixture 30 grams of aluminium chloride were added. A reaction began in about half an hour, and soon hydrogen chloride was evolved in large quantities. After twenty-four hours the solution was decanted from the double aluminium compound, which was washed with carbon disulphide to remove the excess of chlorbenzene. The residue was decomposed with ice and extracted with carbon disulphide. The filtered extract was dried over calcium chloride and fractionated under a pressure of 38 mm. After the removal of the solvent, the product distilled over at 205°–220°, and a small quantity of a tarry substance remained in the flask. The oil, when redistilled at 38 mm., boiled at 217°–219° (corr.). About 14 grams were obtained. A large amount of chlorbenzene was recovered, and it was evident that the reaction was not complete. If the reaction had proceeded longer a better yield would probably have resulted. The substance was a pale-green, very viscid liquid of peculiar odor. It was soluble in carbon disulphide, petroleum ether, and ether, slightly soluble in cold alcohol, and insoluble in water. It dissolved readily in hot, dilute alcohol and 4,4′-dichlorbenzophenone crystallized out in brilliant plates on cooling. Cold concentrated sulphuric acid dissolved the oil with the evolution of hydrogen chloride; on dilution the ketone was precipitated.

The high-boiling residue from the fractionation of the substance was extracted with hot alcohol; on cooling, crystals of the ketone separated, together with a small quantity of long, colorless needles, which melted at 66°–68°. The amount of this substance obtained was too small to warrant further study. The 4,4′-dichlorbenzophenone chloride was analyzed by boiling it with dilute alcohol and titrating the hydrochloric acid formed. 23.43 per cent of acid was obtained instead of 23.20, the theoretical amount.

4,4′-*Dichlorbenzophenone.*—This ketone is readily obtained from its chloride by heating with dilute alcohol, or by solution in concentrated sulphuric acid and subsequent dilution. The product so formed was identified with the ketone obtained by Dittrich[1] by the action of *p*-chlorbenzoyl chloride on chlorbenzene and aluminium chloride. It was readily soluble in carbon disulphide, chloroform, ether, glacial acetic acid, and hot dilute alcohol or acetone. When a solution of the ketone in concentrated sulphuric acid is allowed to stand some time in the air, the ketone crystallizes out in plates. It crystallizes from hot dilute alcohol in glistening, pearly plates, which melt at 144°.5. Two determinations of chlorine in the ketone gave 28.21 and 28.29 per cent instead of 27.90 per cent.

4,4′-*Dibrombenzophenone.*—A mixture of 20 grams carbon tetrachloride, 40 grams brombenzene, 30 grams aluminium chloride, and 150 cc. carbon bisulphide was allowed to react at room temperature for two days. The reaction-product was decomposed and treated as described above under the analogous chlorine compound. The dark oil so obtained decomposed with evolution of bromine when an attempt was made to distil it under diminished pressure. It resembled in its chemical properties the analogous chlorine derivative, and from it was obtained 4,4′-dibrombenzophenone, which was identified with the compound obtained by Hoffmann from brombenzoyl chloride and brombenzene. The ketone melts at 171°–172°. It is soluble in carbon bisulphide, chloroform, benzene, and in hot alcohol or acetone; it is less readily soluble in ether and acetic acid. A determination of bromine gave 47.22 per cent; the theory requires 47.06 per cent.

2,5,2′,5′-*Tetrachlorbenzophenone Chloride.*—20 grams *p*-dichlorbenzene and 6.5 grams carbon tetrachloride were dissolved in 100 cc. carbon bisulphide and 10 grams aluminium chloride were added. There was no reaction at room temperature. After the mixture had been boiled for ten hours the carbon disulphide was filtered off and evaporated to crystallization. Fifteen grams of *p*-dichlorbenzene were recovered. The aluminium compound was decomposed with water and extracted with carbon disulphide. The filtered extract deposited, on evaporation, a mass of brilliant, colorless crystals. As the compound is very soluble in carbon disulphide it was found that crystals could be obtained more readily by adding alcohol and then by boiling to get rid of most of the carbon disulphide. On cooling, the substance crystallizes out in leaflets. In this way 5 grams of 2,5,2',5'-tetrachlorbenzophenone chloride, melting at 173°–174°, were obtained. The yield was good since but 5 grams of dichlorbenzene entered into the reaction. In later experiments the quantity of dichlorbenzene which was used up was materially increased by heating the reaction-mixture for two days and adding small portions of aluminium chloride from time to time.

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[1] Ann. Chem. (Liebig), 264, 175.

The tetrachlorbenzophenone chloride dissolves easily in chloroform, benzene, and acetone, less readily in ether, and very slightly in hot alcohol and concentrated sulphuric acid. An analysis gave the following results:

0.2333 gram substance gave 0.5306 gram AgCl (Carius).

	Calculated for $(Cl_2C_6H_3)_2CCl_2$.	Found.
Cl	56.80	56.46

The ketone chloride is converted into the corresponding ketone by boiling with dilute alcohol, or more quickly by heating in a sealed tube to 130° with dilute alcohol or water. The chloride is much more stable than the two ketone chlorides described above.

2,5,2',5'-Tetrachlorbenzophenone. — Several grams of the ketone chloride were boiled with dilute alcohol for four hours under a return condenser. The solution was filtered hot from unchanged chloride. On cooling, large, feathery plates separated, which on recrystallization from alcohol melted sharply at 128°. The original mother-liquor was found to contain hydrochloric acid. The crystals were colorless and very brilliant. They dissolved readily in hot alcohol, petroleum ether, carbon disulphide, benzene, acetone, ethyl acetate, and chloroform; less easily in cold alcohol and concentrated sulphuric acid. The analysis agreed with the composition calculated for tetrachlorbenzophenone.

0.2560 gram substance gave 0.4611 gram AgCl.

	Calculated for $(Cl_2C_6H_3)_2CO$.	Found.
Cl	44.37	44.53

The ketone was obtained more rapidly by heating the chloride with a mixture of 1 part alcohol and 3 parts water in a tube, at 130°, for two hours. The ketone was separated from any unchanged chloride by treatment with hot alcohol in which the chloride is almost insoluble.

BOSTON, MASS., August 1, 1901.

XXXIV.—ON THE PREPARATION OF TRIPHENYLMETHANE.

BY JAMES F. NORRIS AND GRACE MACLEOD.

A short time ago[1] the results of some work done in this laboratory on the condensation of carbon tetrachloride with benzene in the presence of aluminium chloride were published. Friedel and Crafts[2] and E. and O. Fischer[3] had previously studied this reaction and had obtained triphenylmethane as the result. We obtained, however, a nearly theoretical yield of triphenylchlormethane. The difference in the result was due to the fact that the earlier workers had distilled the reaction-product, whereas we had purified it by crystallization, care being taken to prevent any decomposition.

As it was evident that, in this case, distillation had resulted in the complete destruction of the true product of the reaction, it seemed important to examine other condensations in such a way that the actual result of the reaction might be isolated. We first undertook to study carefully the preparation of triphenylmethane from chloroform, benzene, and aluminium chloride.

The crude reaction-product has always been distilled in this preparation, and beside the expected hydrocarbon other compounds are obtained in appreciable quantities. It has been observed by those who have studied this reaction, that at a certain point in the distillation, hydrochloric acid is given off, and at the end a carbonaceous residue is left. The reaction-product evidently contains a halogen compound, which is decomposed during the distillation.

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[1] Norris and Saunders: This JOURNAL, 25, 54.

[2] Compt. rend., (1877), p. 1453.

[3] Ann. Chem. (Liebig), 194, .

From an examination of the cases in which the Friedel and Crafts reaction has been applied to polyhalogen compounds, and the products of the condensation have been isolated by crystallization, it was evident that the normal reaction consisted in only a partial elimination of the halogen atoms. Carbon tetrachloride gives with benzene triphenylchlormethane, with toluene tritolylchlormethane, and with *p*-dichlorbenzene, tetrachlorbenzophenone chloride. Phenyl iodidedichloride gives diphenyliodonium chloride, and the unsymmetrical chloride of *o*-sulphobenzoic acid gives a compound which contains one chlorine atom. It seemed of importance, therefore, to determine whether the conclusion is warranted which is indicated by these examples, namely, that in the Friedel and Crafts reaction polyhalogen compounds do not lose all of their halogen atoms during the condensation. The investigation of this question appeared worth while, as in many cases compounds containing two or more halogen atoms linked to the same carbon atom have given abnormal results when condensed with hydrocarbons, *e. g.*, unsymmetrical tetrabromethane gives symmetrical tetraphenylethane together with a number of unexpected products.

A condensation of chloroform and benzene was effected according to the directions of Friedel and Crafts. The reaction-mixture was boiled in order to bring about the elimination of as much hydrogen chloride as possible. The aluminium addition-product was decomposed carefully with ice in the presence of a large quantity of carbon disulphide in order to prevent any decomposition of the true product of the reaction. The solution so obtained was dried over calcium chloride and was allowed to evaporate in a current of air. After most of the solvent was removed a dark-brown oil remained, from which crystals separated slowly. At the end of about six weeks, over one-half of the product had been obtained in crystalline condition, and an oil was left which did not crystallize on further standing. All attempts to obtain crystals from this oil were without success. The result of the experiment was surprising as not a trace of triphenylmethane was found. The crystals proved to be triphenylcarbinol, and the oil was readily soluble in cold concentrated sulphuric acid, in which triphenylmethane is insoluble.

On account of this unexpected result the experiment was repeated a number of times under different conditions, but in every case with the same results. In order to find out if, in our experiments, the condensation had taken place in the usual way, the product of a reaction was divided into two portions,—about three-fourths was subjected to distillation and one-fourth was crystallized and tested for triphenylmethane. When distillation was used a good yield of the hydrocarbon, together with some diphenylmethane, was obtained. Crystallization produced the same results as before. These experiments showed conclusively that the triphenylmethane which is obtained in this reaction is the product of the destructive distillation of a mixture of substances which does not contain the hydrocarbon.

We, accordingly, undertook to discover by what reactions triphenylcarbinol was formed, and to determine what substances were present in the uncrystallizable oil. The simplest explanation of the formation of the carbinol appeared to be that at first the three chlorine atoms in the chloroform were replaced by phenyl groups in the usual way, and then the resulting triphenylmethane was converted into the carbinol by the oxygen of the air in the presence of aluminium chloride. The oxidation of a hydrocarbon to a hydroxyl compound in this way was shown to be possible by Friedel and Crafts, who converted benzene into phenol by the action of oxygen in the presence of aluminium chloride. With triphenylmethane, however, the phenomenon is different in that the hydrogen oxidized is joined to a methane carbon atom.

The action of oxygen on the hydrocarbon and aluminium chloride was accordingly studied. Friedel and Crafts have already noted the fact that the chloride decomposes triphenylmethane in part when the substances are heated together. Heated at 120° for ten minutes, the hydrocarbon becomes resinous and yields some benzene. If warmed for ten hours, at 70°, with 7.5 parts of benzene and 1 part of the chloride, diphenylmethane is formed. No details of the experiments are given, but it is probable that the reaction-products were distilled.

In the experiments made by us, a solution of triphenylmethane in carbon disulphide was treated with aluminium chloride in the cold. The chloride slowly extracted the hydrocarbon from the solvent and was thus converted into a brown, gummy mass. After standing about two days this mass was separated and was washed a number of times with carbon disulphide to remove any triphenylmethane that had not reacted with the chloride. The intermediate product was decomposed by ice and the organic part was extracted. On evaporation of the solvent a resinous substance was obtained from which no crystalline material could be separated. The product dissolved in concentrated sulphuric acid in the cold, and therefore contained no triphenylmethane. The experiment showed that even in the cold, triphenylmethane is decomposed by aluminium chloride.

A second series of experiments was made under the same conditions as the first, with the exception that air was drawn through the mixture. After careful decomposition the organic part was taken up in carbon disulphide, and the solution was dried and evaporated in a current of air. The product resembled that obtained in the first experiments from chloroform, benzene, and aluminium chloride. Crystals of triphenylcarbinol separated in appreciable quantity and a thick oil, soluble in sulphuric acid, was left. It is evident from this experiment that triphenylmethane is converted into triphenylcarbinol and a product that cannot be brought to crystallization when it is treated with aluminium chloride and oxygen.

A portion of the reaction-product of this last experiment was treated with sulphuric acid after the solvent had been removed by evaporation. Solution took place with the evolution of hydrogen chloride. When this solution was poured into water, triphenylcarbinol was formed. The evolution of hydrogen chloride during the solution of the reaction-product was evidence of the presence of some organic halogen compounds in the mixture. This compound was shown to be triphenylchlormethane. An experiment showed that aluminium chloride converts triphenylcarbinol into triphenylchlormethane. A solution of the pure carbinol in carbon disulphide was treated with the chloride. The dark gummy compound which was formed was decomposed by ice and then extracted. The solution so formed was dried and evaporated in a stream of dry air. Crystals were obtained which melted indistinctly near the melting-point of triphenylchlormethane. It was impossible to purify the substance by recrystallization as the chloride is readily converted into the carbinol. The impure material was accordingly boiled with alcohol to convert any triphenylchlormethane present into the corresponding ether. A sufficient quantity of the ether was obtained in a pure condition and identified. The work, therefore, proves that triphenylmethane is converted by air, in the presence of aluminium chloride, in part into triphenylcarbinol, and that this, in turn, is to some extent changed into triphenylchlormethane.

An attempt was next made to determine what substances were present in the oil which was formed along with triphenylcarbinol from chloroform and benzene. This oil, which was present to the extent of nearly 50 per cent, could not be brought to crystallization in any way. It seemed possible at first that it might contain diphenylmethane, triphenylmethane, diphenylchlormethane, diphenylcarbinol, triphenylchlormethane, benzhydrol ether, or triphenylcarbinol. It dissolved in sulphuric acid in the cold with slight evolution of hydrogen chloride. When this solution was poured into a large volume of water, a precipitate was formed in small quantity. This precipitate was shown to be triphenylcarbinol.

The action of cold sulphuric acid on the substances mentioned above was studied. The hydrocarbons were insoluble after standing a day in contact with the acid. Triphenylcarbinol dissolved readily and was precipitated quantitatively on dilution. Triphenylchlormethane dissolved with evolution of hydrogen chloride and gave the carbinol on dilution. Diphenylcarbinol and benzhydrol ether were insoluble, and diphenylchlormethane dissolved with evolution of hydrogen chloride. The test with sulphuric acid showed that the chief constituent of the oil was not one of the substances enumerated above.

On account of the fact already mentioned that a number of polyhalogen compounds give products in this reaction which contain halogen, a search was made for diphenylchlormethane. A portion of the heavy oil was distilled with steam. A few drops of a light-yellow oil were found in the distillate. When treated with ice this substance solidified to crystals which melted at 22° to 23°. The compound which contained chlorine, upon standing some days in contact with water, changed into another free from halogen, and hydrochloric acid was found in solution. Diphenylchlormethane might act in this way, but Engler,[1] who has described this compound, gives its melting-point as 14°. A sample prepared by us by the method of Engler melted at 18° to 20°. It is possible that the substance was a small quantity of diphenylchlormethane which distilled over without decomposition by the steam. Nearly the entire amount of the original oil was apparently unchanged. It was soluble in sulphuric acid as before, but the distillation flask contained a trace of hydrochloric acid.

To test the behavior of diphenylchlormethane with steam, about 2 grams of it were distilled. A very small quantity of diphenylcarbinol passed over with the steam. The product left in the distillation-flask was shown to be benzhydrol ether, which was found to be insoluble in sulphuric acid. The original oil, therefore, could not have contained more than a trace of diphenylchlormethane.

These experiments show that the oil was, in all probability, a complex condensation-product. As it could not be purified it was studied, side by side, with the similar oil obtained by the action of air on a mixture of triphenylmethane and aluminium chloride. Both oils dissolved in sulphuric acid, and the solutions so formed exhibited a strong fluorescence when diluted. These solutions appeared to be identical as far as the experiments were carried. They were heated to boiling, neutralized with barium carbonate, and filtered. The filtrates showed a beautiful blue fluorescence and gave barium salts on evaporation. These salts were soluble with great difficulty, even in boiling water. As no crystals could be obtained and we had no proof that the substances were chemical individuals, they were not studied farther.

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[1] Ber. d. chem. Ges., 7, 1128.

In conclusion, it appears from the work that the process by which triphenylmethane is obtained from chloroform is a very complex one, in which a number of unexpected reactions take place. The hydrocarbon is probably produced as a result of the reduction of the intermediate product, triphenylcarbinol, by the uncrystallizable oil, which is completely decomposed during the distillation.

The results also indicate that a thorough study of the condensations of other polyhalogen compounds with hydrocarbons in the presence of aluminium chloride, would probably furnish an explanation of the abnormal results which have been obtained heretofore in nearly every case.

BOSTON, MASS., August 1, 1901.

Contributions from the Chemical Laboratory of Bryn Mawr College.

ON SOME COMPLEX COMPOUNDS OF THALLIUM, AND THE CONSTITUTION OF DOUBLE SALTS.

BY ALLERTON S. CUSHMAN.

I.

In a recent number of this JOURNAL[1] there was published a paper by the writer, entitled "On Some Isomeric Compounds of Thallium, and the Constitution of Double Salts." This paper bore the date of acceptance for publication of May 15th. In the July number of the *Zeitschrift für anorganische Chemie* appeared a comprehensive article by Richard Jos. Meyer, entitled "Beiträge zur Kenntnis des dreiwerthigen Thalliums," which bore the date of acceptance of May 29th. In so far as these two papers cover the same ground, there would have been no question of priority were it not for the fact that much of the work presented by Meyer had been carried out by C. Wiegand, and published by him as a dissertation, entitled "Über Halogenverbindungen des Thalliums" (Berlin, 1899). As there was at that time no index to dissertational literature, it is not surprising that the author was quite unaware that he had been in a measure anticipated in the field. The priority of Wiegand in having first prepared some of the chlorobromides and bromochlorides has been conceded by the author in a note to the "Chemiker Zeitung."[1] The responsibility, however, of the claim for isomerism, as well as the actual existence and constitution of some of the compounds, still remains with the present writer. After the appearance of the above-mentioned papers, it was early pointed out that certain discrepancies in some of the points presented required clearing up. Wherever discrepancies occur in the presentation of matters of scientific fact it is natural to assume that one or the other must be altogether right; there are, however, other possible explanations. In some cases both may be in a sense right and only the interpretation at fault, while, as a final possibility, both may be wrong. It is to be hoped that any discrepancies that come under discussion here may be considered as falling under the second case.

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[1] This JOURNAL, **24**, 3.

The study of sesquihalogen compounds is alluring on account of the promise it holds out of shedding light on the much vexed question of inorganic structure, but, on the other hand, it is surrounded with great experimental difficulties. The ease with which these compounds undergo hydrolysis or decomposition, their hygroscopic nature, their mixed equilibria in relation to water of crystallization and state of oxidation, and their generally complex nature, present dangerous pitfalls to the investigator.

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[1] Chem. Ztg., (1900), I, 3.

Perhaps the most serious divergence of view between Meyer and the writer lies in the fact that the former has been led to the belief that, in solution, thallic chloride behaves as though it had the structure $(TlCl)Cl_2$. Such a view is not only fatal to certain facts and theories already put forward, but also casts doubt upon a great mass of analytical data, by implying that the chlorine in thallic chloride cannot be completely precipitated by silver nitrate. As a result of previous and recent work the author is of the opinion that such a view is untenable, and that Meyer was led to it by a misinterpretation of certain analytical results. Since this point is of vital importance, it will now be necessary to examine the evidence. In order that the facts which led Meyer to form his opinion may be fully presented, it is necessary to quote him verbatim: "Interessant ist das Verhalten des Thalliumchlorids in stark salpetersaurer Lösung, in einer Lösung also, in der die Hydrolyse stark zurückgedrängt oder ganz aufgehoben ist. Eine Reihe von Fällungsversuchen hat nämlich gezeigt, dass in der salpetersauren Lösung des Thalliumchlorids sowie seiner Kaliumchloriddoppelsalze das Chlor durch Silbernitrat in der Kälte nur teilweise gefällt wird. * * * * Ich wurde zuerst auf diese Thatsache aufmerksam, als ich versuchte, das Chlor in Thalliumchlorid und seinen Doppelsalzen titrimetrisch nach der Volhard'schen Methode zu bestimmen. Hierbei machte man die Erfahrung, dass von den drei Atomen des Chlorids im Maximum nur zwei Atome an Silber gebunden wurden. Diese unvollkommene Fällbarkeit des Thalliumchlorids in salpetersaurer Lösung, lässt bezüglich der Konstitution des Thalliumchlorids zwei Deutungen zu." Here follows some discussion which may be omitted, but which concludes with the words: "Man wird vielmehr annehmen, dass das Thalliumchlorid in nicht hydrolysierter Lösung im Sinne der Formel $(TlCl)Cl_2$ reagiert." Later on in his paper Meyer takes up the point again. After describing the usual Volhard method of procedure, he gives some of his results and shows that in each case only about two-thirds of the total amount of chlorine present is precipitated as silver chloride, and although the results are not quantitative, they seem to show, at least qualitatively, that one of the three atoms of chlorine is held by the thallium. Finally, Meyer seems to be satisfied with his conclusions for he terminates the discussion by saying: " Ich beabsichtige, diese Fällungsversuche auch auf die Chloride anderer dreiwertiger Metalle auszudehnen."

In repeating Meyer's work with the Volhard method, the fact was confirmed that the percentage of chlorine found never fully represented the total amount present, but it was noted that in each titration a very faint odor of hydrocyanic acid was discernible. Further experiment showed that when solutions containing thallic ions are mixed with solutions of potassium sulphocyanate, potassium cyanide is formed. On referring to the literature it was found that as early as 1858 Pean de Saint-Gilles[1] proved that when solutions of sulphocyanate are treated with oxidizing agents the following reaction takes place:

$$2RCNS + 2H_2O + O_6 = 2RCN + 2H_2SO_4.$$

No one will doubt that thallic ions are strong oxidizing agents, and as potassium cyanide is undoubtedly formed, we have a conclusive explanation of the incomplete precipitation of silver chloride. Meyer himself noted that when first reduced with sulphurous acid the precipitation of the chloride was complete. The author has frequently carefully examined the filtrates from the usual gravimetric determinations, where, of course, no sulphocyanate is used, and no sign of incomplete precipitation of the chlorine has yet been observed. Thus the evidence which supports the writing of thallic chloride as $(TlCl)Cl_2$, as well as all speculation from this point of view, falls to the ground.

At the present time it is difficult to entertain any theory of the structure of inorganic compounds that does not in some way account for the relation of molecules of water of crystallization to the general configuration of the larger molecule.[2]

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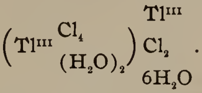
[1] Jsb. Chem., (1858), p. 585.

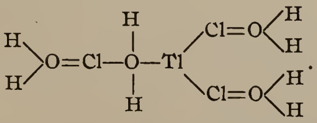
[2] In the discussion of these theories, a word is constantly needed to distinguish between the smaller and the larger molecule, thus, thallic chloride is stable only when associated with 4 molecules of water. In this paper the "thallic chloride molecule" is used to designate $TlCl_3$, while the stable hydrate $TlCl_3.4H_2O$ will be called the "thallic chloride complex." Where more than one hydrate exists the saturated condition will be so designated, the other being the "lower complex."

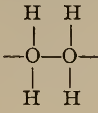
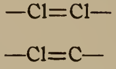
In Werner's theory this is done by assuming that molecules of water that cannot be removed by desiccation, or without destroying the molecule, are contained within the nucleus. Thus, as there is some evidence to show that one of the four molecules of water in the thallic chloride complex is differently related to it from the other three, this fact would have to be expressed by Werner's theory as follows:



$$\left(\mathrm{Tl^{III}}\begin{matrix}\mathrm{Cl_4}\\ \mathrm{(H_2O)_2}\end{matrix}\right)\begin{matrix}\mathrm{Tl^{III}}\\ \mathrm{Cl_2}\\ \mathrm{6H_2O}\end{matrix}.$$

Under the valence theory, as ordinarily written, water of crystallization has never been considered, or accounted for. Granting, however, that oxygen can be quadrivalent, which allows water under certain circumstances to behave as an unsaturated molecule, then we have in hand a valence theory which seems to be capable of giving a satisfactory explanation of a great mass of facts. It is as allowable to assume molecules of water entering into the internal structure of a complex as it is to suppose them in some mysterious way externally attached. To explain the thallic chloride complex, under this theory we should write:



It will be seen that, according to this way of writing, the full saturation value for water, of molecules of the type RCl_3 is six. This is known to be true in the cases of aluminum, iron, and other trivalent atoms, although there is no reason why the fully saturated form should in all cases be the stable one. No thallic chloride complex with six molecules of water has ever been isolated. Kohler has shown[1] that aluminum chloride in water solution, or in any solvent that is known to combine with it, has the molecular weight corresponding to the formula $AlCl_3$, whereas in a saturated indifferent solvent like carbon bisulphide it has the double molecular weight. It will be seen that these facts are accounted for by this theory. The linkage  $-\overset{H}{\underset{H}{O}}-\overset{H}{\underset{H}{O}}-$ is not strong enough to hold the large complex together while the linkage  $\begin{array}{c}-Cl=Cl-\\ -Cl=C-\end{array}$ is. It may be said, in conclusion, that this theory which has grown out of much friendly discussion between Professor Kohler and the author is advanced here simply to the extent that it seems to offer a satisfactory explanation of the constitution of the thallium complexes.

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[1] This Journal, 24, 5.

It is not, of course, assumed that this possibility of quadrivalent oxygen is presented here for the first time. It has often been used before, especially to account for the structure of peroxides and persulphates. Moreover, there can be no doubt of the fact that the evidence so far advanced, bearing on such a general theory as the unsaturated character of the water molecule in the formation of hydrated salts, is insufficient. The suggestion is made here only in view of the author's intention to carry the inquiry further.

II.

EXPERIMENTAL PART.

Thallium forms halogen compounds of three definite stages of oxidation, $TlCl$, Tl_4Cl_6, and $TlCl_3$. As would be expected, the stability of these three compounds is in the reverse order of their respective solubilities. The first two may be called difficultly soluble compounds. Their character and structure have been fully discussed in the author's first paper.[1] Anhydrous thallic chloride, on the other hand, is extremely soluble, not only in water but in most solvents, notably alcohol and ether. It is, however, very hygroscopic and unstable, and it may fairly be doubted if it has ever been prepared in the perfectly anhydrous and unreduced state. Meyer has claimed that he prepared and analyzed it, but repeated efforts made in this laboratory to prepare it in a state fit for analysis and molecular weight determination, have ended in failure. Two water complexes of thallic chloride have been described by Werther,[1] and by Meyer,[2] corresponding respectively to the formulae $TlCl_3.4H_2O$ and $TlCl_3.H_2O$. In order to study the main complex of thallic chloride, a compound was prepared by a method somewhat similar to that adopted by Meyer. Pure thallous chloride was suspended in water, and chlorine was passed in until the oxidation was complete and a clear solution of thallic chloride was obtained. This was evaporated on a water-bath, at 80°, until nearly ready to crystallize, a little more chlorine was then passed in and the mother-liquor left to crystallize spontaneously. In this way beautiful orthorhombic crystals were obtained, some of them measuring more than a centimeter along the major axis. These crystals were crushed, dried by careful pressing between layers of blotting-paper, and analyzed. Meyer describes the crystals which he obtained as being very hygroscopic. These crystals were not at all hygroscopic but, on the contrary, could be left for days exposed to the air, in which case they usually lost a trifle owing to air-drying. In desiccators over various drying agents, the complex begins to lose water at once, as will shortly be shown. The results of the analysis of these crystals is given below, and in order to show that they were probably identical with Meyer's preparation his results are printed in parallel.

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[1] *Loc. cit.*

1.7730 grams substance yielded 1.8866 grams Tl_2PtCl_6.
1.0053 grams substance yielded 1.1263 grams AgCl.

	Theory for $TlCl_3.4H_2O$.	Found.	Meyer found.
Tl	53.38	53.26	54.36
Cl	27.78	27.70	27.48

Meyer dried his substance before analysis for twenty-four hours over sulphuric acid and caustic potash; that this is not permissible is shown by a glance at the accompanying curve

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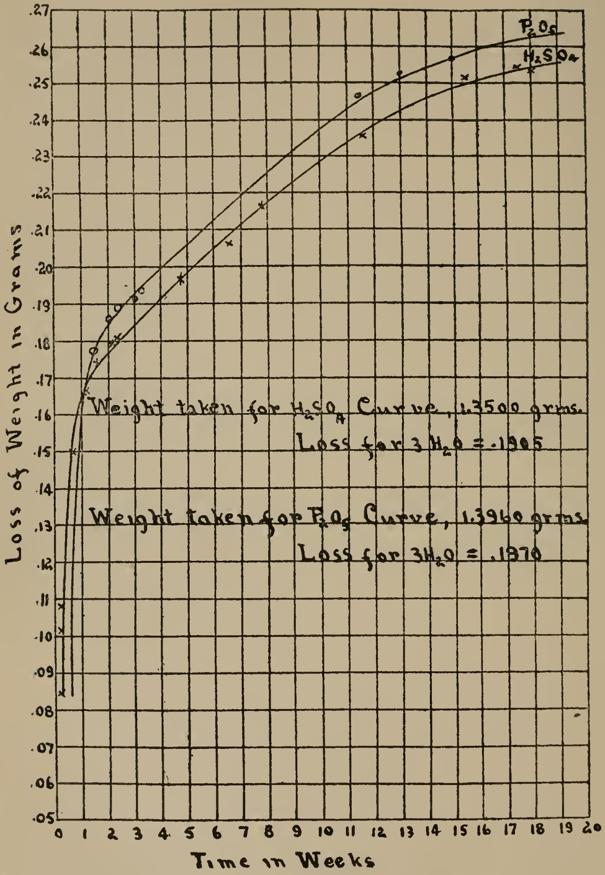
[1] J. prakt. Chem., **91**, 385 (1864).

[2] Ztschr. anorg. Chem., July, 1900.



shown in the figure. In the experiment from which this curve was plotted, two lots of the paper-dried crystals were weighed in separate watch-glasses and immediately shut up in large desiccators containing, respectively, sulphuric acid and phosphorus pentoxide. Weighings were made at first every few hours, then every day, and finally every week. The experiment lasted twenty-one weeks, and the rate and order of the loss in weight are fully shown by the plotted curves. The axis of abscissae shows the time in days and weeks, the axis of ordinates, the loss in weight. At the conclusion of the experiment the substances were still very slowly losing weight, owing to loss of chlorine. The complex does not pass the monohydrate condition without losing chlorine. Both Werther and Meyer claim to have isolated the monohydrate, but the author has never succeeded in doing so. The curves both show rather sharp turns, and it may be taken as certain that the last fourth of the water comes off slowly, accompanied by chlorine, but the evidence for the definite monohydrate stage is slight, to say the least. In this connection Meyer says: "Die Entwässerung des Tetrahydrats wurde im Luftbade bei 55° vorgenommen und die Gewichtsabnahme von Stunde zu Stunde festgestellt. Hierbei gehen drei Moleküle Wasser kontinuierlich fort, ohne dass Reduction des Chlorids eintritt. 1.9814 g. nahmen 0.2625 g. ab. Berechnet für 3 Mol. H_2O: 0.2800 g. Bei weiterem Erhitzen beginnt die Schmelze sich gelb zu färben, und es tritt Geruch nach unterchloriger Säure auf. Die Gewichtsabnahme schreitet dann nur äusserst langsam vorwärts. Nach weiterem 2½-stündigem Erhitzen auf 55°, betrug der Verlust nur noch 0.01 g., im Exsiccator blieb das Gewicht dann auch nach 20-stündigem Trocknen konstant."

It will be noted that the existence of a definite monohydrate stage exactly suits the quadrivalent oxygen theory, although it is not demanded by it, since it is equally possible that as soon as the outside protecting water molecules are taken off, chlorine and the last molecule of water begin to leave simultaneously.

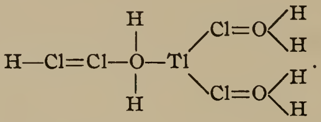
The next piece of evidence is interesting and important. Meyer has shown that when the preparation of the thallic chloride complex is attempted in the presence of hydrochloric acid by a method similar to the one described above, a definite crystalline compound is obtained corresponding to the formula $TlCl_3.HCl.3H_2O$. Meyer compares this to a compound of gold, and he writes them respectively,

$$HTlCl_4 + 3H_2O \quad \text{and} \quad HAuCl_4 + 3H_2O.$$

He further points out that they may thus be considered as acid anhydrides which, by combining with 1 molecule of water, lead to the acid hydrates,

$$H_2TlCl_5O \quad \text{and} \quad H_2AuCl_5O.$$

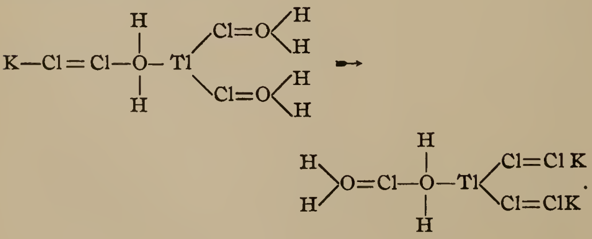
According to the quadrivalent oxygen theory, we might write:



Meyer has described the character of this compound as follows: In dry air it is very stable, but on heating it undergoes reduction with simultaneous loss of water, hydrochloric acid, and chlorine. In solution it reacts strongly acid, and on neutralization with potassium hydroxide and subsequent evaporation it yields crystals, not of the salt $KTlCl_4.xH_2O$, as might be expected, but the definite compound $TlCl_3.2KCl.2H_2O$ according to the equation:

$$2(TlCl_3.HCl) + 2KOH = TlCl_3.2KCl + TlCl_3 + 2H_2O.$$

According to our theory, the rearrangement of the complex is expressed as follows:



It can be inferred from this that the linkage which was strong enough to attach H—Cl to the complex in a certain position is not stròng enough to hold the heavier and more basic K—Cl, and thus a redistribution is brought about, the products naturally being the most stable ones possible under the circumstances. Unfortunately, lack of time has not permitted the study of the dehydration of this compound in this laboratory, but the theory would enable us to predict that this compound should lose without reduction but 1 molecule of water. According to Meyer, "dieses Salz giebt beim Erhitzen auf 50° to 60° und im Vakuum-exsiccator, nur ein Molekül Wasser ab. Weitergehende Entwässerung führt auch hier zu Reduction."

One of the peculiarities of thallic chloride and its water complex is the ease with which they dissolve in most solvents, including ether and alcohol. When the thallic chloride complex is dissolved in ether, and the ether evaporated in a current of cold dry air, a crystalline product is obtained. With reference to this product the author finds himself in some disagreement with Meyer. In this laboratory, when dried crystals of the compound $TlCl_3.4H_2O$ were dissolved in pure ether, the liquid divided into two layers—a water solution below and an ether solution above. If the two layers are separated and evaporated, both deposit crystals which resemble each other in appearance and have almost identically the same composition. Meyer, apparently, did not note the formation of the two layers, but obtained, by direct evaporation of the solution of the thallic chloride complex in ether, large, glistening, hexagonal crystals, which he analyzed and represented by the formula $TlCl_3.(C_2H_5)_2O$,—in a word, a thallic chloride complex with 1 molecule of ether of crystallization. Meyer's data are given as follows:

	Calculated for $TlCl_3.(C_2H_5)_2O$.	Found.
Tl	53.09	52.73
Cl	27.64	26.75
Ether	19.27	20.57
	100.00	100.00

It would seem to be a most extraordinary phenomenon if 4 molecules of water in the stable complex could be directly replaced by 1 molecule of ether. If this, indeed, were true, there would be but one way of proving it and that is by making a combustion of the compound. Unfortunately, Meyer made no combustion but determined the ether by difference. It is difficult to see what became of the water in Meyer's preparation, or how his analysis proves the constitution which he publishes, since the compound $TlCl_3.4H_2O$ has a percentage composition almost identical with that of the compound $TlCl_3.(C_2H_5)_2O$. In the author's work, the ether layer was evaporated as described above, until crystallization had progressed to a certain point; the mother-liquor was then poured off and the crystals redissolved in anhydrous ether. This operation was repeated twice, and the final crop of crystals was drained and dried by repeated pressing on blotting-paper. These crystals were analyzed with the following results:

1.5829 grams compound yielded 1.6866 grams Tl_2PtCl_6.

0.8614 gram compound yielded 0.9746 gram AgCl.

	Calculated for		
	$TlCl_3.(C_2H_5)_2O$.	$TlCl_3.4H_2O$.	Found.
Tl	53.09	53.38	53.31
Cl	27.64	27.78	27.97

From this analysis it seemed doubtful whether any ether compound was formed at all, and it was quite possible that the water complex was simply crystallizing from the ether solution. Manifestly an organic combustion was necessary to decide the point. A combustion was therefore carefully made, a long layer of lead chromate in the combustion tube insuring the complete absorption of the halogen. The results were as follows:

1.5224 grams substance taken yielded 0.2722 gram H_2O and 0.0585 gram CO_2. From these results it is calculated that 0.0236 gram of ether and 0.2419 gram of water were present in the original substance, and we have for the whole analysis:

Tl	53.31
Cl	27.97
H_2O	15.89
Ether	1.55
	98.72

It is apparent from this analysis that the ether has only very slightly replaced the water in the complex, and indeed it may be doubted whether the water has been replaced at all, since a certain quantity of ether is sure to have been included in the crystals. Meyer states that anhydrous thallic chloride is easily prepared by putting this "ether compound" in a vacuum. A preparation of anhydrous thallic chloride being desired in order that its molecular weight might be determined in different solvents, 20 grams of the substance which had been twice recrystallized from ether were put into a vacuum desiccator over phosphorus pentoxide, and connected with a Sprengel pump. In order to reduce the danger of reduction of the compound, the whole desiccator was placed inside of a refrigerator so that the temperature at no time rose above 18°. For twenty days a fairly good vacuum was maintained. At the end of that time the phosphorus pentoxide had absorbed enough water from the substance to become quite wet. Whatever the compound remaining in the dish may have been, it certainly was not anhydrous thallic chloride. Exposed to the air it was very hygroscopic, but it no longer completely dissolved in anhydrous ether, and gave every evidence of having suffered a partial reduction. Meyer has also described a compound of the formula $TlCl_3.C_2H_5OH$, which he obtained by dissolving the water complex in absolute alcohol, and crystallizing by evaporating the solution *in vacuo*. Since a compound with this formula would have a thallium and chlorine content quite different from that of the water complex, it should be a comparatively easy matter to determine its composition. The author has never made this compound.

The discussion of any further discrepancies between the work of the author and other investigators must be reserved until more work has been done. The pressure of other work has not permitted a thorough reexamination of all the compounds described in the first paper, nor does it seem that good can come from an investigator repeating his own work. The writer sees no more reason to doubt the isomerism of the chlorobromides and bromochlorides of thallium at the present time than he did a year ago. In conclusion, it may be stated that in so far as it has seemed necessary in this paper to discuss the work of another investigator, there has been no intention of doing more than is demanded by the effort to get at the truth about these interesting and important compounds. If the author has in any way been led into errors or misinterpretations of results, the criticism which is sure to follow will be welcomed with interest. It is recognized that the truth is the important thing, and that a mere matter of opinion is of no value whatever.

ON THE DECOMPOSITION OF HYDROGEN PEROXIDE BY VARIOUS SUBSTANCES AT HIGH TEMPERATURES.

BY J. H. KASTLE AND MARY E. CLARKE.

The oxidation of an alkaline solution of chromic oxide to potassium chromate by hydrogen peroxide is one of the well-known reactions of the latter substance. In making a few observations on this oxidation with the view of making chromic oxide the acceptor in the study of certain oxidations by means of atmospheric oxygen, it occurred to one of us (Kastle) to test the conduct of aqueous hydrogen peroxide towards chromic hydroxide in neutral or faintly acid solution. On heating small amounts of the chromic hydroxide with 3 per cent hydrogen peroxide it was observed that oxygen was evolved with an active effervescence when the solution of the peroxide was heated nearly to its boiling-point.

In this connection it occurred to us to test the conduct of a number of other well-known substances towards the peroxide, particularly those, of course, which have no action upon this substance in the cold. As may be seen from the following, certain of these substances catalyzed the peroxide rapidly at 100° C., whereas others were apparently without action upon it at this temperature.

Substances which catalyzed hydrogen peroxide at 100° C.	Substances which do not catalyze hydrogen peroxide at 100° C.
Ferrous sulphate	Sodium chloride
Iron ammonium alum	Sugar
Cupric chloride	Magnesium sulphate[1]
Ferric hydroxide	Zinc oxide
Barium peroxide	Thymol
Copper oxide	Mercuric oxide
Cadmium iodide	Cadmium sulphide
Copper sulphate	Aluminium hydroxide
Potassium dichromate	Oxalic acid
" chromate	
Platinic chloride	
Potassium chlorplatinate	
Cobalt sulphate	
Nickel "	

So far as we have been able to discover in the literature upon this subject, no systematic attempts have ever been made to determine the conduct of substances of different types towards hydrogen peroxide at high temperatures. In his earlier work upon the peroxide, Thénard[2] seems to have reached the conclusion that all substances exert some effect on the peroxide; some, like the acids, to increase its stability; others, like the oxides of metals and finely divided metals, to decompose it.

In 1890 Tammann[3] found that the spontaneous decomposition of hydrogen peroxide in alkaline solution is independent of the nature of the base, and that it is probably brought about by means of certain metallic oxides, such as the oxides of iron, dissolved in the alkali. He observed that the addition of small amounts of such oxides increases the rate of decomposition enormously. Hanriot,[4] Wolffenstein,[5] and others have found that dilute solutions of hydrogen peroxide can be concentrated by heating on the water-bath; in fact, the latter has found that hydrogen peroxide is relatively stable when heated, provided the solution is free from alkaline compounds, and derivatives of the heavy metals, and solids of all kinds, even those that are chemically indifferent.

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[1] On trying magnesium sulphate more carefully it was found to yield small quantities of oxygen by heating it with the peroxide.

[2] Ann. chim. phys., **9**, 317 (1818).

[3] Ztschr. phys. Chem., **4**, 441.

[4] Compt. rend., **100**, 57, 172.

[5] Ber. d. chem. Ges., **27**, 3307.

Quite recently Manchot and Wilhelms,[1] in a communication "On the Peroxide of Iron and the Catalytic Action of Iron Salts," have shown that a solution containing ferrous sulphate and hydrogen peroxide yields considerable quantities of oxygen.

Aside from these few more or less isolated observations, however, we have not been able to find that any study has been made of the action of different substances on hydrogen peroxide at high temperatures. It seemed desirable, therefore, to measure the several amounts of oxygen liberated from hydrogen peroxide at 100° C., or thereabouts, by various substances. This was effected in the following manner: 5 cc. of hydrogen peroxide were placed in a wide-mouth bottle of medium size (175 cc.) and the required amount of the substance, whose action on the peroxide was to be tested, was placed in a small bottle of about 6 cc. capacity, and 5 cc. of water added. This small bottle was then placed in an upright position in the large bottle containing the given quantity of hydrogen peroxide. This large bottle was then tightly stoppered with a single-hole rubber stopper, fitted with a gas-delivery tube, and placed in a bath which was kept filled with boiling water. The gas-delivery tube was then connected with a gas burette. After the level of the water in the gas burette had come to rest, the substance to be tested was brought into the peroxide by slightly tilting and shaking the bottle so as to upset the smaller bottle. The water in the bath was kept actively boiling, and after a certain period the amount of gas in the gas burette was determined. Except when expressly stated to the contrary Marchand's 15-volume solution of hydrogen peroxide, diluted with an equal volume of water, was employed in these experiments. Five cc. of this solution were found to yield 69 cc. of oxygen with lead peroxide and sulphuric acid, temperature 23° C. and 745 mm. pressure.

Five cc. of this solution were used in each experiment, and the substances whose effect on this were to be studied were employed in the proportion of the thousandth part of their molecular weight in grams, dissolved in 5 cc. of boiling water. The reaction therefore proceeded at a dilution of 10 cc. The results of our experiments, together with all necessary data regarding them, not already mentioned, are given in the following table:

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[1] Ber. d. chem. Ges., 34, 2485.

Table I.

Substance used.	Quantity of substance. Gram.	cc. oxygen evolved.	Time.	Temperature. Degrees C.	Pressure.
Water		5.5	15 min.	31	744
Copper sulphate	0.249	44.5	15 "	24.5	725
Cobalt "	0.2811	37.5	15 "	26.5	738.5
" "	"	38	15 "	26	737.5
Nickel "	0.2807	50	15 "	26	"
" "	"	46	15 "	24	739.5
Cobalt ammonium sulphate	0.3951	38.5	15 "	25	"
Cobalt ammonium sulphate	"	40.5	15 "	26	"
Cobalt ammonium sulphate	"	38.5	15 "	26	"
Nickel ammonium sulphate	0.3947	26	15 "	25	"
Nickel ammonium sulphate	"	24.3	15 "	"	"
Ferrous ammonium sulphate	0.392	32.5	15 "	26	"
Ferrous ammonium sulphate	"	32.2	3½ "	"	"
Iron amm'n'm alum	0.964	39.5	15 "	"	746
" " "	"	38.5	10 "	"	"
Potassium alum	0.9484	23	15 "	"	"
" "	"	21.5	15 "	"	"
Potassium chromic alum	0.9983	38	15 "	"	"
Potassium chromic alum	"	38.5	15 "	"	"
Potassium chloride	0.0746	5.5	15 "	27	"
" "	"	7.5	15 "	"	"
" bromide	0.1190	7.5	15 "	"	"
" "	"	7	15 "	"	"
" iodide	0.162	40.5	15 "	26	"
" "	"	38	1 "	"	"

Substance used.	Quantity of substance. Gram.	cc. oxygen evolved.	Time.	Temperature. Degrees C.	Pressure.
Water (alone)	....	8	15 min.	27	745
Zinc sulphate	0.2784	7.5	15 "	"	"
" "	"	9	15 "	"	"
Magn's'm sulphate	0.246	15	15 "	"	"
Ferrous "	0.278	42	15 "	"	"
Manganese "	0.277	30	15 "	"	"
Silver nitrate	0.170	28	15 "	28.5	"
Sodium "	0.085	16	15 "	"	"
Lead peroxide and sulphuric acid	....	56.86	15 "	24	732
Cane sugar	0.342	6.5	15 "	"	"
Sodium chloride	0.0585	7	15 "	"	"
" "	"	8	15 "	"	"
Potassium dichromate	0.2945	46	15 "	26	746
Potassium chromic alum	0.001	20	15 "	27	747
Potassium chromic alum	"	19	15 "	26	"
Cobalt potassium sulphate	0.4373	49.5	15 "	"	"
Cobalt potassium sulphate	"	51	15 "	"	"
Cobalt potassium sulphate	"	54	16 "	27	"
Nickel potassium sulphate	0.4369	25.5	15 "	"	"
Nickel potassium sulphate	"	23.5	15 "	"	"
Benzoyl peroxide	0.242	8	15 "	26	"
Thallous chloride	0.239	18	15 "	27	"

Considerable differences have been observed in the mode of action of a number of these substances. For example, the iron salts, potassium iodide, and chromic alum decompose hydrogen peroxide with great rapidity, whereas, in the case of other substances, such as the nickel and cobalt salts, the rate of decomposition is much slower, although ultimately it is nearly as great. That this is true will be seen from the following table:

Table II.

Substances.	Gram.	Time. Minutes.	Oxygen evolved. cc.
Copper sulphate	0.249	1	37
" "	"	2	41
" "	"	15	44.5
Ferrous ammonium sulphate	0.392	1	31.5
" " "	"	2	32
" " "	"	15	32.5
Iron ammonium alum	0.964	½	39
" " "	"	2	39.5
" " "	"	3	39.5
" " "	"	15	39.5
Potassium iodide	0.162	½	39
" "	"	1	40
" "	"	15	40.5

Among the substances which decompose the peroxide more gradually we have the following:

Potassium chromic alum	0.9983	½	7.5
" " "	"	1	14
" " "	"	2	20
" " "	"	15	38
Nickel sulphate	0.2807	1	6
" "	"	2	14
" "	"	15	46
Cobalt sulphate	0.2811	2	6
" "	"	15	37.5
Cobalt ammonium sulphate	0.3951	1	5
" " "	"	2	11.5
" " "	"	15	38.5
Manganese sulphate	0.277	1	0
" "	"	2	7
" "	"	15	30

The decomposition of the peroxide by certain of these substances, at least, seems to be a true catalysis. This is notably the case with copper sulphate and potassium dichromate, very small amounts of which effect the decomposition of the peroxide. The effect of varying amounts of copper sulphate and potassium dichromate may be seen from the following table:

Table III.

Quantity of copper sulphate used. Gram.	Oxygen evolved. cc.	Time. Minutes.	Temperature. Degrees C.	Pressure.
0.249	44.5	15	24	744.5
0.1245	44	15	25	"
0.0622	44.3	15	28	"
0.0249	44.6	15	27	"
0.0010	44.5	15	27	"
0.0001	38.5	15	28.5	738.5
0.00002	23.1	15	26.5	743
0.00001	18	15	27.5	"

Quantity of potassium dichromate used. Gram.	Oxygen evolved. cc.	Time. Minutes.	Temperature. Degrees C.	Pressure.
0.2945	46	15	26	746
"	45.6	15	27	"
0.0736	45.5	15	26	"
"	44.8	15	26	"
0.001	45.5	15	27	"
"	49	15	26	"
0.00002	15	15	27	"
"	17	15	27	"

When it is borne in mind that all of our experiments were carried out in a total volume of 10 cc., it is evident that 1 part of copper sulphate and 2 parts of potassium dichromate per million are sufficient to effect the decomposition of the peroxide at 100° C.; and about the only difference that could be observed in the action of the copper sulphate and potassium dichromate at different dilutions was that at greater dilutions the decomposition proceeded much more slowly than with large amounts of these compounds. Some idea of the difference in the rate of decomposition may be gathered from the following:

Quantity of copper sulphate. Gram.	Time. Minutes.	Oxygen evolved. cc.
0.249	1	37
"	2	41
"	15	44.5
0.1245	1	19
"	2	23

Quantity of copper sulphate. Gram.	Time Minutes.	Oxygen evolved. cc.
0.1245	15	44
0.0622	1	32
“	2	36
“	15	44.3
0.001	1	21
“	2	34
“	15	44.5
0.0249	1	31
“	2	42
“	15	44.6

With smaller amounts than 0.001 gram :

0.0001	1	6
“	2	10.5
“	15	38.5
“	23	50.8
0.00002	1	2
“	2	5.5
“	15	23.1
“	20	27
“	23	33
0.00001	1	1.5
“	2	2.5
“	15	18

From the comparatively few cases thus far studied it is impossible to arrive at any general conclusions concerning the cause of these decompositions of hydrogen peroxide, and a great deal more work will have to be done before we can hope to elucidate the matters here under consideration. It is interesting to note, however, in this connection, that of those substances that are capable of causing the decomposition at 100° C. some of them, such as potassium iodide and ferrous sulphate are chemically acted on by the peroxide, and most of those that cause the decomposition of the peroxide contain elements, such as copper and iron, that are capable of combining with oxygen in several different proportions. It may be, therefore, that these several substances capable of bringing about the decomposition of hydrogen peroxide, first combine with it to produce an even more unstable derivative than the hydrogen peroxide itself, and that this then decomposes into oxygen, water, and the substance originally causing the catalysis; or looked at from a slightly different point of view, an unstable peroxide may be formed by the action of the hydrogen peroxide on the catalyser, which, by its decomposition, gives oxygen and the original substance. In this connection it is interesting to note that in the decomposition of hydrogen peroxide by finely divided copper a certain interval elapses after bringing these two substances together before the decomposition begins, and during this interval the metallic copper becomes black. This points to the formation of copper peroxide as preliminary to the catalysis of hydrogen peroxide by finely divided copper. A similar explanation has recently been advanced by Manchot and Wilhelm[1] to account for the catalytic action of iron salts on hydrogen peroxide. It would seem probable from these observations that a great many substances will be found capable of decomposing hydrogen peroxide at high temperatures, whereas a great many others will doubtless be found to exert no influence on the decomposition of this compound. To determine just what kinds of substances will and what will not effect this decomposition, and to determine also, if possible, the cause of such decomposition would seem to offer a large and fruitful field for further investigation. It is our intention, therefore, to make a thorough study of these phenomena.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Oct., 1901.

PHENOLPHTHALIN AS A REAGENT FOR THE OXIDIZING FERMENTS.

BY J. H. KASTLE AND O. M. SHEDD.

In spite of the large amount of work that has been done on the oxidizing ferments since their existence in the living cell was first pointed out by Schönbein[2] in 1856, and later by Traube in 1877,[3] their conduct has been tried towards comparatively few reducing agents. The oxidation of hydroquinone and certain other phenols and of salicylic, benzoic, and formic aldehydes, the production of guaiacum-blue from guaiacum resin, or better from guaiaconic acid, the synthesis of indophenol and similar dyestuffs, the color reaction with guaiacol, and the oxidation of arsenious to arsenic acid, are the principal changes brought about by the oxydases that have been investigated to any extent. In view of this and of the fact that phenolphthalin is readily oxidized to phenolphthaleïn, a substance readily and beautifully lending itself to colorimetric measurements, it occurred to one of us (Kastle) that this leuco-compound might possibly prove a valuable reagent in the study of the oxidizing ferments.

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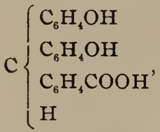
[1] Ber. d. chem. Ges., **34**, 2479.

[2] Schaer: "Die neuere Entwickelung der Schönbeinschen Untersuchungen über Oxydationsfermente." Ztschr. f. Biol., **37**, 321 (1899).

[2] Ber. d. chem. Ges., **10**, 1895 (1877).

Phenolphthalin, or dioxytriphenylmethanecarbonic acid,



$$C\left\{\begin{array}{l} C_6H_4OH \\ C_6H_4OH \\ C_6H_4COOH \\ H \end{array}\right.,$$

was first obtained by Baeyer[1] in his investigation of the phthaleïns. The compound is readily prepared by reducing phenolphthaleïn, in alkaline solution with zinc dust. It may thus be obtained in the form of a white crystalline substance. According to Baeyer, phenolphthalin is a strong acid. It is almost insoluble in water, but dissolves readily in alkalies with the formation of readily soluble salts, and on boiling with water it readily dissolves the carbonates of the alkaline earths. In solution it is rapidly oxidized by the more powerful oxidizing agents such as potassium ferricyanide and permanganate, and even on exposure to air it is slowly oxidized to phenolphthaleïn.

On testing the conduct of phenolphthalin towards aqueous liver extracts, which are known to contain at least one oxidase, *viz.*, aldehydase, no certain results could be obtained, and while the results of our experiments are not as yet accepted as absolutely conclusive, they seem to indicate that the oxidation of phenolphthalin is not accelerated by the hepatic ferments.

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[1] Ann. Chem. (Liebig), **202**, 80.

The conduct of phenolphthalin towards the potato was next tested. According to Traube, the potato contains an oxidizing ferment. This is shown by the fact that aqueous extracts of the potato give guaiacum-blue directly, without the intervention of hydrogen peroxide or ozonized turpentine. Indeed, the conduct of tincture of guaiacum towards the different parts of the potato tuber is exceedingly interesting. If the potato is scraped and the alcoholic solution of guaiacum applied to the fresh surface just beneath the skin, the characteristic blue color is developed immediately; on the other hand, if the guaiacum is applied to the freshly cut surface of the inner parts of the tuber, the blue color does not show itself at once, but develops slowly on standing exposed to the air. It has also been observed that if a potato is cut in two and guaiacum applied to one surface but not to the other, and both left exposed to the air, the one to which the tincture of guaiacum has been applied slowly develops a blue color, whereas the other does not develop the power to turn guaiacum blue directly as one might suppose, but requires fully as much time to develop the blue color as the freshly cut surface. Aqueous extracts, both of that portion of the tuber immediately beneath the cuticle and of the pulp, turn guaiacum blue at once. It is not the purpose of the present communication, however, to enter into a discussion of the exact significance of these results.[1] As surmised by Traube, however, they certainly seem to point to the presence of an oxidizing ferment in the tuber. It occurred to us, therefore, that an extract of the potato, especially of the epidermal portions of the tuber, might prove a suitable solution on which to test the conduct of phenolphthalin, our mode of procedure being as follows: The outer scrapings of 2 or 3 potatoes, of this season's growth, were macerated with water and the mixture filtered and made up to 25 cc. with water. Clear, yellowish-brown solutions were thus obtained, 5 cc. of which required 0.15 cc. N/20 NaOH in order to give a permanent pink color to phenolphthaleïn.

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[1] These and other results reached in the study of oxidations effected by vegetable and animal tissues will be more fully discussed in a subsequent communication.

Tubes were then prepared containing 5 cc. of this extract together with 1 cc. of a solution of sodium salt of phenolphthalin.[1] These tubes were then allowed to stand at the ordinary temperature for certain intervals, at the end of which 1 cc. of N/20 solution of sodium hydroxide was added. With the potato extracts employed this quantity was ample to insure an excess of alkali. Under these conditions, if any of the phenolphthalin had been oxidized, the characteristic color of phenolphthaleïn was developed on the addition of the alkali. Further, the intensity or depth of this color was an approximate measure, at least, of the extent of the oxidation in any case. In the following the conditions of the experiments, together with the results obtained, are given in detail.

Three tubes were prepared, the contents of which were as follows:

I. 5 cc. of water and 1 cc. of phenolphthaline solution.

II. 5 cc. extract of potato scrapings boiled and 1 cc. of phenolphthalin.

III. 5 cc. extract of potato scrapings and 1 cc. of phenolphthalin.

These three tubes were allowed to stand for half an hour at room temperature, at the end of which time 1 cc. N/20 sodium hydroxide was added to each, with the following result:

Color after Addition of 1 cc. N/20 Sodium Hydroxide.

I. Very faint pink.
II. Yellowish-brown, with just the faintest tinge of pink.
III. Dark-red.

Precisely similar results were obtained with another extract of potato scrapings, in which case the tubes were allowed to stand at the ordinary temperature for an hour before the addition of the alkali. On adding the N/20 sodium hydroxide the water control in this set of experiments showed a faint pink color, the boiled extract a yellowish-brown with a faint pink tinge, the active, unboiled extract a dark-red.

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[1] The solution of phenolphthalin employed in this investigation was prepared in the following manner: 0.05 gram of phenolphthalin was mixed with just enough N/20 sodium hydroxide to dissolve it. A small quantity of phenolphthalin was then added in order to make certain of neutralizing any slight excess of alkali. The solution was then made up to 10 cc. with water and filtered through a dry filter. A perfectly clear, colorless solution of the sodium salt of phenolphthalin was thus obtained, which was found to be perfectly neutral both to litmus and phenolphthaleïn.

Similar results were obtained with still a third extract. In this series of experiments the tubes were allowed to stand seventeen hours at room temperature. On adding 1 cc. of N/20 sodium hydroxide, the water control showed a decided pink color, the boiled extract gave a yellowish-pink color, and the active extract a dark-red.

Essentially similar experiments have been tried repeatedly since these first experiments were performed, and in every case active, freshly-prepared extracts of the cuticle of the potato oxidized phenolphthalin.

The Stability of the Oxidase of the Potato in Aqueous Solutions.

As yet no attempt has been made to isolate the oxidase of the potato, and in the extracts employed in this investigation it probably occurs in association with quite a number of substances, among them some very powerful reducing agents. It is therefore not surprising that these aqueous extracts of the potato soon loose their oxidizing power. That such is the case may be gathered from the following experiments bearing upon this point. Two tubes, I. and II., were prepared, I. containing 5 cc. of freshly prepared extract of the potato (cuticle) and 1 cc. of phenolphthalin. The tube was allowed to stand an hour at ordinary temperature, when 1 cc. of N/20 sodium hydroxide was added. A dark-red color was produced. Tube II. was made with the same extract after it had stood at ordinary temperature for an hour. It also contained 5 cc. of the extract and 1 cc. of phenolphthalin. After standing one hour 1 cc. N/20 sodium hydroxide was added. A light-red color was produced, by no means as dark as the color obtained with Tube I. This indicates a falling off in the oxidizing power of the potato extract even in so short a time.

A second extract of the potato cuticle was prepared at 3.20 P.M., August 13th. The extract gave a splendid dark-blue with fresh guaiacum, and when allowed to act on phthalin in the usual manner it gave a clear, decided phenolphthaleïn-red in one-half hour, and dark-red in one hour. At 4.55 P.M., the same day, the extract still gave the guaiacum reaction, but much less distinctly than at first; and on testing with phthalin for one-half and one hour it gave only a faint pink color in one-half hour and a much lighter red in one hour than when first tested.

In twenty hours and thirty minutes another extract, which had been preserved from putrefaction by thymol and which, when fresh, was quite active, had lost its power both to oxidize phenolphthalin and to turn guaiacum blue.

On the other hand, an extract which had been preserved with thymol for nine days, still gave a pale-blue color with guaiacum at the end of this time. Unfortunately, not enough of this extract was at hand to test its activity towards phenolphthalin.

These results certainly go to show, that on standing at ordinary temperature the extract of the potato rapidly loses its power to oxidize phenolphthalin and guaiacum.

With the view of determining the solubility of the ferment in other solvents besides water, a quantity of potato scrapings was allowed to dry in the air for twenty-four hours at ordinary temperature. The dry mass was ground to a fine powder with coarse white sand, and an aqueous extract prepared and filtered. The clear filtrate gave a clear blue color with guaiacum, not as deep in tint, however, as that produced with the fresh extracts. Its activity toward phenolphthalin was tested in the usual manner. After an hour's action on the phthalin it showed a decided pink color on the addition of 1 cc. N/20 sodium hydroxide. This color was by no means as deep, however, as that obtained with the fresh extracts in the same length of time. The loss of activity on the part of the tissues, after removal from the tuber is by no means as great, however, as that sustained by the active aqueous extracts in the same length of time.

The Distribution of the Oxidase in the Potato.

As already pointed out above, that part of the potato tuber immediately beneath the skin gives the blue color with guaiacum at once, whereas a freshly cut surface through the pulp only gives the blue color after standing in contact with guaiacum for some time. On the other hand, aqueous extracts both of the outer scrapings of the potato and of the pulp give the guaiacum-blue at once. This would seem to indicate its universal distribution of the oxidase throughout the tissues of the tuber. With the view of testing the correctness of this conclusion, an aqueous extract of the potato pulp was prepared by thoroughly macerating it with water. Five cc. of this extract required 1.5 cc. N/20 sodium hydroxide to produce a permanent pink color with phenolphthaleïn. It gave a light-blue color with guaiacum at once. Three tubes were prepared, each containing 5 cc. of the extract and 1 cc. phthalin. The extract in one of these tubes was boiled and cooled to ordinary temperature before adding the phthalin, in order to serve as a control. After twenty minutes, 2.5 cc. N/20 sodium hydroxide were added to one of the active tubes and also to the control. The latter showed no trace of pink color, whereas the active tube showed a decided clear pink. The second tube was allowed to stand twenty minutes longer. Two and a half cc. of N/20 sodium hydroxide were then added. A decided red color was produced, slightly deeper in tint than that obtained with the tube that had stood twenty minutes. There can be no doubt, therefore, that the oxidase is present in the starchy pulp of the potato, as well as in the hypodermal layers. Traces of it have even been found in the harder, denser portions of the skin. This was shown by carefully removing the skin of the potato and washing and scraping thoroughly so as to remove any of the hypodermal tissues. The skin was then allowed to dry in the air for twenty-four hours, when it was ground to a fine powder with coarse white sand. The powder was then extracted with water and the extract filtered. The filtrate gave a very faint-blue with guaiacum. In order to test its activity towards phenolphthalin, a tube was prepared containing 5 cc. of the extract with 1 cc. phthalin. This was allowed to stand one hour. One cc. N/20 sodium hydroxide was then added, when a very light-pink coloration was produced. A control experiment showed no coloration in the same length of time. It is evident, therefore, that even the skin of the potato contains small amounts of the oxidase.

Effect of Time on the Oxidation of Phenolphthalin by the Oxidase of the Potato.

Even the oxidation of guaiacum by the potato oxidase, while very rapid, is still by no means an instantaneous process, and the oxidation of the phthalin proceeds much more slowly. One advantage of phenolphthalin over a number of substances hitherto proposed as reagents for the oxidases is that the rate of oxidation can be easily and accurately determined by colorimetric comparisons with alkaline solutions of phenolphthaleïn of known strength. While we have not yet had an opportunity to do this, a sufficient number of comparisons has been made to indicate that up to a certain limit, at least, the amount of phenolphthalin oxidized is proportional to the time of its remaining in contact with the oxidase. This may be seen from the following experiments: Tubes were prepared containing 5 cc. of a freshly prepared extract of potato scrapings and 1 cc. phthalin. These were allowed to stand for different intervals, at the end of which 1 cc. N/20 sodium hydroxide was added and the color noted. The following results were obtained:

Time.	Color produced on addition of N/20 NaOH.
1 min.	Scarcely perceptible
5 "	Distinctly pink
15 "	Light-pink
30 "	Decided pink
60 "	Dark-red

It will be seen that the amount of oxidation is proportional to the time. It should be noted in this connection that the oxidation apparently reaches a maximum in one hour. Tubes that have stood for even twenty-four hours give no darker red on the addition of the alkali than those that have stood for an hour. This would indicate either that the oxidase is inhibited in its action by the products of the reaction, or that the oxidizing ferment is really some unstable oxygen compound which by its decomposition oxidizes the reducing agents which are present. The presence of such a compound in the living cell would account satisfactorily for the oxidation of a limited amount of phenolphthalin.[1]

The Influence of Air on the Oxidation of Phenolphthalin by Potato Oxidase.

In this connection one would naturally be led to inquire whether it is the oxygen of the air which oxidizes the phthalin, the oxidase acting simply in the capacity of an oxygen carrier, or whether the oxygen is supplied by the .oxidase itself.

In order to determine, therefore, whether the potato oxidase is an oxygen carrier or merely an unstable oxidizing agent, tubes were prepared, each containing 5 cc. of a freshly prepared potato extract and 1 cc. phthalin. Two tubes were allowed to stand undisturbed in the usual manner for fifteen minutes and one hour, respectively. Through a second pair of tubes a current of air was passed for fifteen minutes and one hour, respectively. The two tubes that had been allowed to run for fifteen minutes showed no difference in color on the addition of 1 cc. N/20 sodium hydroxide; and of the two tubes that had been allowed to run for one hour, the one which had stood quietly during this time gave a somewhat darker tint on the addition of 1 cc. N/20 sodium hydroxide than the tube through which the current of air had passed. From this it would seem that the oxidase of the potato is not an oxygen carrier in the ordinary sense in which this term is employed.[2]

The Occurrence and Distribution of the Potato Oxidase.

This particular oxidase which turns guaiacum blue directly and oxidizes phthalin, is by no means confined to the potato tuber, but is widely distributed, especially in the vegetable kingdom. As yet, the only animal secretion in which we have found it is human saliva. Without entering into all of the experimental details, there is given in the following table the results of our search for this oxidase in vegetable and animal tissues. In every case aqueous extracts or solutions were employed, and 5 cc. of the extract used in each experiment, together with 1 cc. of the phenolphthalin solution. The acidity of every extract and solution was determined previous to the experiment, in order to know just how much N/20 caustic soda should be added to render the liquid alkaline at the conclusion of the test. It should be observed in this connection that all vegetable extracts used in these experiments had an acid reaction. Hence the oxidation of the phenolphthalin took place in acid solution, and the results in the following table are given for such solutions only. It was observed, however, that the oxidation of phenolphthalin takes place most rapidly in slightly alkaline solutions, and in using this substance as a reagent for the oxidizing ferments it may be well, especially with extracts of weak oxidizing power, to work in alkaline solution. In such solutions, however, it should be borne in mind that the control experiments do not remain colorless even for comparatively short intervals, but always develop a pink color, lighter, of course, in tint than the active extract. This is due to the fact that the oxidation of phenolphthalin by air alone proceeds far more rapidly in alkaline than in acid or neutral solutions. In our experiments the conduct of every extract was also tested towards a fresh alcoholic solution of guaiacum as well as towards phenolphthalin; and all experiments were checked by suitable controls. The results obtained are set forth in the following table:

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[1] Further work on this part of the subject is now well under way in this laboratory. The results of the investigation will be embodied in a separate communication by Kastle and Loevenhart.

[2] It should be observed in this connection, however, that in 1848 Schönbein (*Cf.* Schaer : Ztschr. f. Biol., **37**, 32 (1899)) showed that air is necessary for the production of guaiacum blue by the potato. This has been confirmed in this laboratory. It would seem, therefore, that while air is necessary for the production of the oxidizing ferment, the latter cannot transfer unlimited amounts of atmospheric oxygen like a true oxygen carrier. The exact significance of this peculiar conduct on the part of the oxidizing ferment of the potato will be discussed in the subsequent communication, to which reference has already been made above.

Table I.

Substance.	Color with guaiacum.	Duration of exp. with phthalin.	Vol. N/20 NaOH added.	Color produced by N/20 NaOH.
1. Ipomoea Batatas :				
Sweet potato, skin	Dark-blue	40 min.	1 cc.	Dark-red
" " "	"	60 "	1 "	"
2. Zea Mais :				
Silk of green corn	Blue	30 "	1 "	Pink
" " " "	"	60 "	1 "	Deeper pink than obtained in 30 minutes
3. Musa sapientum :				
Banana, pulp, ripe	Blue	30 "	2 "	Pink
" " "	"	60 "	2 "	More pink than in 30 minutes
4. Gum arabic	Blue	2 hours	1 "	Decided pink
5. Gum tragacanth	Very faint-blue	2 "	1 "	Very light-pink
6. Cherry tree gum, fresh	Light-blue	2 "	1 "	Decided pink
7. Pine tree gum, fresh	Very faint-blue	4 "	1 "	Slight but decided pink
8. Lycopersicum esculentum Tomato, green fruit	None	17 "	4 "	None
9. Allium Cepa : Onion, bulb	None	7 "	2 "	None

Table I (Continued).

Substance.	Color with guaiacum.	Duration of exp. with phthalin.	Vol. N/20 NaOH added.	Color produced by N/20 NaOH.
10. Malt, infusion, fresh	Light-blue	5 hours	2 cc.	Faint pink
11. Agaricus campestris: Common mushroom	None	4½ “	1 “	None
12. Lepiota Morgani	Dark-blue	1 hour	1 “	Pink
13. Nicotiana Tabacum: Tobacco, Kentucky Burley	Dark-blue	½ “	1 “	Pink
14. Glycinehispida: Soy bean, pod	Dark-blue	1 “	1 “	Dark-red
“ “ stem	“	15 min.	1 “	“
15. Dioscorea divaricata (Cinnamon vine): Axillary tubers	Dark-blue	½ hour	1 “	Dark-pink
16. Saliva, human	Pale-blue	3 hours	1[illegible] “	Decided pink
17. Testicle of sheep	None	20 “	2[illegible] “	None

It will be observed that there is a complete parallelism between the oxidation of guaiacum and phthalin by active extracts of living tissues. An extract which gives a deep-blue color with guaiacum will oxidize more phthalin in a given time than one which shows only a faint blue with the former reagent. For example, the potato and sweet potato give a darker blue with guaiacum and oxidize more phthalin in a given time than the silk of the maize or saliva. Further, substances which do not give a blue color direct with guaiacum do not oxidize phenolphthalin at all. Examples of this kind, among plants, are the onion and tomato, and among animal tissues, the liver and testicle of the sheep. In this connection it is interesting to note that those vegetable tissues which readily turn guaiacum blue and oxidize phthalin, readily turn brown or reddish in color when their freshly cut surfaces are exposed to the air; such, for example, are the potato, sweet potato, and banana; whereas, those tissues which do not turn guaiacum blue or oxidize phthalin, such as those of the onion and tomato, do not alter in color when their freshly cut surfaces are exposed to the air. This is in confirmation of the views of Lindet,[1] who believes the darkening of apple juice to be due to an oxidase which oxidizes the tannin of the fruit.

Further, our experiments would seem to indicate that the oxidase concerned in the bluing of guaiacum and the oxidation of phthalin is not identical with the catalase recently described by Loew;[2] for this reason the power of any of these tissues to decompose hydrogen peroxide is not at all proportional to its power to oxidize either guaiacum or phthalin. For example, aqueous extracts of hog liver, sheep testicle, and the common mushroom decompose hydrogen peroxide with the greatest vigor, whereas none of them act upon guaiacum or phthalin; on the other hand, the fresh, green leaf of the tobacco decomposes hydrogen peroxide slowly, whereas it oxidizes guaiacum and phthalin rapidly.[3]

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[1] Compt. rend., **120**, 370 (1895).

[2] U. S. Department of Agriculture, Report No. 68.

[3] On the other hand, Spitzer (Pflüg. Arch., **67**, 615 (1897)) is of the opinion that the oxidation of salicylic aldehyde and the decomposition of hydrogen peroxide, by

In conclusion it may be said that, from the results already obtained, it would seem that phenolphthalin will prove a valuable reagent in the study of oxidation processes in animals and plants. It certainly affords a beautiful method for demonstrating the presence of certain oxidases.

State College of Kentucky,
Lexington, August, 1901.

ON THE NATURE OF CERTAIN OF THE OXIDIZING FERMENTS.

By J. H. Kastle and A. S. Loevenhart.

In a series of remarkably interesting investigations extending over a period of nearly twenty years (1848–1867), Schönbein[1] demonstrated the occurrence of oxidases (Sauerstofferreger and Sauerstoffträger) in a large number of plants and also in certain animal tissues. Somewhat later, in 1877, Traube[2] introduced the conception of oxidizing ferments. According to Traube these oxidizing ferments are of two kinds, *vitale* and *faulige*, or those operating in higher living organisms and those present in dead matter. Among the first he included the guaiacum-bluing ferment of the potato and the coloring-matter of the red blood corpuscle. Since then the subject of the oxidizing enzymes and the part played by them in oxidations in the living cell has claimed the attention of a large number of observers. Among the oxidations studied in this connection may be mentioned the synthetic oxidation of naphthol and *p*-phenylenediamine to indophenol by Ehrlich; the syntheses of certain indamines and eurhodines by Rohmann and Spitzer; the production of a garnet-red coloring-matter from guaiacol by Bourquelot; the formation of quinone from hydroquinone by laccase, a ferment first obtained by Yoshida, and more completely investigated by Bertrand; and lastly, quantitative measurements of the rate of oxidation of salicylic aldehyde, first by Schmiedeberg and his pupils, and

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animal extracts at least, are due to the same cause. On the other hand, E. Lepinots (Compt. rend. de la Soc. de Biol., May 26, 1899) did not observe a parallelism to exist between the quantities of oxygen developed from hydrogen peroxide and the intensity of other reactions, as that upon guaiacum and guaiacol, etc.

[1] See résumé of Schönbein's work by Schaer: Ztschr f. Biol., 37, 321 (1899).

[2] Ber. d. chem. Ges., 10, 1985 (1877).

later by Medwedew and by Jacoby. Besides the work of Schönbein these probably include the more important investigations that have been undertaken in this field.

Except for the work of Bertrand on laccase, Jacoby on salicylase, and Loew on catalase, few if any attempts have been made to isolate the oxidizing ferments, and apart from their destruction by heat and a few poisons, but little is known concerning them which would lead us to regard them as of an enzymic nature. In fact, they do not seem to act as oxygen carriers at all in the sense of being able to transfer large amounts of oxygen from the air to the oxidizable substance. Medwedew observed in his study of the oxidation of salicylic aldehyde to salicylic acid by animal tissues, that this oxidation cannot be increased by an increase in the amount of oxygen present; in other words, this oxidation is independent of the presence of air. He is therefore of the opinion that the oxygen required for such oxidations is derived either from oxyhæmoglobin or from proteid (Pflüger's intramolecular oxygen).

Then, again, it seems never to have been satisfactorily established that the oxidations effected by the so-called oxidases are really catalytic processes in the true sense, *viz.*, that a very small quantity of the substance can, in the presence of free oxygen, effect the oxidation of a relatively large amount of the oxidizable substance. In this connection, however, it should be mentioned that Jacoby[1] has shown in his recent investigation of aldehydase that if the salicylic acid produced is removed by dialysis, the enzyme still possesses some activity. Unless the aldehydase were present in very large quantities in Jacoby's solutions, or these contained unusually large amounts of active intramolecular oxygen, these results of Jacoby are somewhat difficult to reconcile with those obtained by Medwedew, in which he found that atmospheric oxygen was not necessary for the oxidation of the aldehyde.

In attempting to follow the formation of starch in the sprouts and growing tuber of the potato, we had occasion to test different portions of the tuber and sprout with tincture of guaiacum. It is certain that both Schönbein and Traube, and perhaps others before them, were familiar with the fact that the potato causes the bluing of guaiacum. On the other hand, it was observed that different portions of the tuber and sprouts of the potato conduct themselves differently towards the guaiacum. These differences in conduct appeared to warrant further study, as the result of which these observations are submitted.

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[1] Ztschr. physiol. Chem., 30, 134 (1900).

When the skin of the potato is removed and fresh tincture of guaiacum added to the exposed part, a splendid blue color at once appears. On the other hand, if a potato is cut in two and fresh tincture of guaiacum applied to the freshly cut surface, the blue color develops at once, only in a ring immediately beneath the skin. On the pulp of the potato the blue color does not appear at once, but only on standing. After a time, however, the surface of the pulp turns a dark-blue. Extracts of the skin of the potato and of the pulp both give the guaiacum-blue at once. The former extract, however, gives a much darker blue with the same quantities of guaiacum. It has also been observed that if a few drops of an old tincture of guaiacum be applied to the freshly cut surface of the potato, a faint blue is instantly produced. This, however, rapidly fades out, but after a time returns and increases in amount until a dark-blue coating is produced. The substance producing the blue color with guaiacum is very soluble in water. Scrapings of the skin of the potato need only to be covered with water for a few minutes and the extract filtered, to give a clear yellowish-brown solution, which instantly gives a dark indigo-blue with fresh tinctures of guaiacum. Such solutions, however, rapidly lose strength, and at the same time become darker brown in color. Weak antiseptics, such as chloroform, toluene, and thymol,[1] tend to preserve the power of such extracts to turn guaiacumblue directly; but even solutions preserved in this manner ultimately lose this property. The following data may be cited as showing the stability of such solutions:

A freshly prepared extract of the outer scrapings of the potato was found to give a deep-blue color instantly with tincture of guaiacum. Four tubes were prepared as follows:

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[1] There is a possibility, of course, that some peroxide may be produced by the slow oxidation of these antiseptics.

No. 1 contained the extract alone.

No. 2 contained the extract, together with a small quantity of chloroform.

No. 3 contained some of the extract simply covered, not shaken, with a layer of toluene about 1 centimeter deep.

No. 4 contained the extract together with a small amount of thymol.

These tubes were allowed to stand exposed to the air for twenty-four hours. At the end of this time 1 cc. of the extract from each of the tubes was drawn out and tested with guaiacum with the following results:

No. 1. No blue color.

No. 2. Blue at once (not as deep a blue as the original).

No. 3. No blue.

No. 4. Blue at once, about same tint as No. 2.

These experiments seem to indicate that the oxidizing substance (ferment) of the potato is unstable, and that its stability is increased by certain antiseptics. Its instability is probably due to the deoxidizing action of the reducing substances present in such extracts. As stated above, these extracts become darker brown in color on standing, and this change of color is ordinarily ascribed to oxidation.

It is interesting to note, in this connection, that those extracts of the potato peel which have lost their power to turn guaiacum blue directly, give the guaiacum reaction again on the addition of hydrogen peroxide. As is well known, a number of extracts of vegetable and animal tissues give a blue color with hydrogen peroxide and guaiacum, which do not give the guaiacum reaction alone. The significance of these results will be discussed in a subsequent part of this paper.

The Nature of the Guaiacum Reaction.

Schönbein, Traube, and the earlier workers in this field seem to have entertained no doubt that the formation of guaiacum-blue is a true oxidation. More recently, however, Nasse and Framm[1] have attempted to show that the bluing of guaiacum tincture does not depend on oxidation by atmospheric oxygen, but must be regarded as a hydrolysis of the guaiacum, since, according to them, this reaction takes place in complete intensity, even when the solutions used are completely freed of oxygen. Hence these observers do not look upon guaiacum as a trustworthy reagent for active oxygen. That oxygen, in some form at least, is necessary for the production of guaiacum-blue seems to have been established by the work of Doebner and Lücker[1] on the guaiacum resin. According to these observers, guaiaconic acid, which composes about 50 per cent of guaiacum resin, yields guaiacum-blue on oxidation, thus:

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[1] Pflüg. Arch., 63, 203 (1896).

$$\underset{\text{Guaiaconic acid.}}{C_{20}H_{24}O_5 + 3O} \quad = \quad \underset{\text{Guaiacum-blue.}}{C_{20}H_{20}O_6 + 2H_2O.}$$

That atmospheric oxygen is essential to the formation of guaiacum-blue by the oxygen carrier (ferment) of the potato has been demonstrated by Schönbein,[2] who showed that the fresh potato in an atmosphere free from oxygen does not give the guaiacum reaction at all. In view of our own ideas upon this subject, and in view, further, of the contradictory statements of Nasse and Framm upon this point which have been referred to above, it seemed to us very important to repeat Schönbein's experiments on this subject. In order, therefore, to determine whether free oxygen is necessary for the guaiacum reaction as brought about by the potato, a potato was placed in a small cylinder, so arranged that a current of hydrogen could gradually replace the atmospheric air which it at first contained. Hydrogen was then passed through the cylinder until all the air had been replaced. The skin of the potato was then scratched by means of a glass rod with sharp edges running through one of the holes of the rubber stopper, closing the cylinder. A drop of fresh guaiacum was then added by means of a separating-funnel without the production of any blue color whatever. The abraided portion of the potato remained white for four hours in the current of hydrogen. The gas was then turned off, the cylinder closed with paraffin, and all rubber connections were fastened tight by means of screw-cocks. In this condition the cylinder containing the potato was allowed to stand seventeen hours, when the abraided portion showed only the faintest blue color. Just as soon, however, as the potato was removed from the cylinder and exposed to the air a dark-blue color developed on the abraided part. The slight bluing observed undoubtedly resulted from leakage. This experiment was repeated several times with similar results.

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[1] Pharm. Arch., **234**, 590 (1896).

[2] Cf. Schaer: *Loc. cit.*

In order to make sure that these effects were not the result of any reducing action on the part of the hydrogen, the same experiments were repeated in carbon dioxide and in nitrogen.

Carbon dioxide was passed through the cylinder containing the potato until the escaping gas was completely absorbed by caustic soda. On scratching the surface of the potato with a glass rod and applying guaiacum, no trace of blue color was developed, even after standing for fifteen minutes. On removal to the air, however, a dark-blue color at once developed on the abraided surface. This experiment was repeated several times with the same result in every case. It was found that, if the potato is scratched and allowed to remain exposed to the air for a very short time before putting it into the atmosphere of carbon dioxide, a delicate blue color appears on the scratched surface. This speedily fades away entirely, in the carbon dioxide, leaving the abraided surface perfectly white. This experiment was also repeated with the same result.

Finally, in order to put the matter regarding the influence of air on the guaiacum reaction beyond doubt, the same experiments were tried in an atmosphere of nitrogen. Accordingly, pure nitrogen was passed through the cylinder containing the potato until the air was displaced. The surface of the potato was then scratched and guaiacum applied. No blue color appeared, and the abraided surface remained white indefinitely. On exposure to air, however, the scratched surface at once turned blue. When the potato was scratched in the air and then put at once into an atmosphere of nitrogen and guaiacum applied, the abraided surface developed a faint blue color which rapidly bleached.

A very simple method of showing the influence of atmospheric oxygen on the bluing of guaiacum by the potato consists in making two parallel scratches on a potato, one some little time before applying the guaiacum, the other immediately before its application. On adding the guaiacum simultaneously to both of the scratched surfaces the one which had been made first developed a dark-blue instantly, while on the other surface the blue color showed more faintly and developed more slowly. These trials were made several times, so that there is no doubt that exposure to the atmosphere for a short time before the application of the guaiacum very markedly accelerates and intensifies the formation of guaiacum-blue.

Taken collectively, these results furnish a certain and convincing confirmation of Schönbein's observations, and leave no room for doubt that free molecular oxygen is essential for the change under consideration. It should also be noted, in this connection, that the formation of guaiacum-blue is not the only oxidation that can be effected by the potato. It also gives the garnet-red color with guaiacol, described by Bourquelot, as characteristic of certain of the oxidases. We have also found an aqueous extract of potato scrapings capable of oxidizing salicylic aldehyde, and in this connection Kastle and Shedd[1] have recently shown that active extracts of the potato have the power of oxidizing phenolphthalin to phenolphthaleïn.

The Conduct of Peroxides towards Guaiacum.

Reference has already been made above to the fact that extracts of potato scrapings which have lost their power to turn guaiacum blue directly, regain their power to do this by the addition of very small amounts of hydrogen peroxide, and yet, ordinarily, hydrogen peroxide alone does not give a blue color with guaiacum. Indeed, the power to give guaiacum-blue with hydrogen peroxide and tincture of guaiacum is characteristic of a large number of plant and animal extracts.[2] It occurred to us, in this connection, to test the conduct of other peroxides towards active animal and plant extracts in the presence of guaiacum. In this work a fresh extract of calve's liver was employed, and it was found that guaiacum-blue was obtained by adding tincture of guaiacum to the liver extract to which a small amount of benzoyl peroxide had been added. Even the boiled liver extract was found to give the guaiacum reaction under these circumstances. It occurred to us, therefore, that the organic peroxides would probably give the guaiacum reaction directly without the intervention of animal or plant extracts at all.

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[1] This Journal, **26**, 528.

[2] Schönbein's test for hydrogen peroxide by means of tincture of guaiacum and extract of malt is based upon this fact.

In order to test this point, benzoyl, phthalyl, and succinyl peroxides were prepared according to the well-known methods of von Pechmann and Vanino, and Vanino and Thiele. Small amounts of these peroxides were shaken with small quantities of distilled water and a drop of tincture of guaiacum added, when, without exception, they gave the guaiacum-blue at once and without the addition of any plant or animal extract at all. These results have been obtained repeatedly both with old and perfectly fresh tinctures of guaiacum, so that there can be no doubt about the conduct of these substances in this respect.

In our first experiments with these organic peroxides, no particular pains were taken to get them in solution. In fact, phthalyl and succinyl peroxides are practically insoluble in all common solvents. In testing them with guaiacum, therefore, they were simply mixed with water, and the tincture of guaiacum added at once. Better results, however, can be obtained in the case of benzoyl peroxide by boiling some of this compound with water, filtering hot, and cooling the filtrate. The latter, which always contains benzoyl peroxide partly in solution and partly in suspension, gives a fine blue color on the addition of guaiacum.

The results obtained with the organic peroxides naturally led us to test the conduct of guaiacum towards certain of the inorganic peroxides and oxides. Accordingly the conduct of lead peroxide, manganese peroxide, silver oxide, and freshly precipitated ferric oxide towards guaiacum was tested by shaking small amounts of these oxides with small quantities of water and adding tincture of guaiacum. Guaiacum blue was obtained at once with the peroxides of lead and manganese, and also with silver oxide, but not with ferric oxide.

These results finally led us to test the conduct of hydrogen peroxide towards tincture of guaiacum. The commercial 3 per cent. solution of hydrogen peroxide does not produce a blue color with guaiacum, either in the cold or on boiling. On heating somewhat more dilute solutions of hydrogen peroxide nearly to boiling and adding guaiacum, a faint blue color was always obtained.

On the Nature of the Oxidizing Ferment of the Potato.

Up to this time the oxidizing ferment of the potato has resisted all attempts to isolate it. This is not surprising when we consider that in all probability it is present in the potato in exceedingly small quantities, and that it is very unstable and remarkably soluble in water. It seems to be insoluble in ethyl and amyl alcohol, at least active extracts of it cannot be prepared by the use of these solvents. It is somewhat soluble in glycerin, but does not seem to be precipitable from either its aqueous or glycerin solutions by alcohol. In view of the fact, however, that both the oxidizing substance of the potato and the organic peroxides give the guaiacum reaction directly, it would naturally suggest itself in this connection that the oxidizing substance in the potato may really be an organic peroxide. It should be observed that, while this supposition is as yet only based upon analogy, it is no idle speculation, but one which best explains the oxidation phenomena exhibited by plants and, in all probability, by animals as well. It should be noted also that Bach,[1] from his studies on the function of peroxides in the phenomenon of slow oxidation, has also reached the conclusion that the so-called oxidizing ferments in the blood are simply readily oxidizable substances having a special aptitude for forming peroxides.

[1] Compt. rend., **124**, 951 (1897).

Conduct of the Oxidizing Ferment of the Potato Towards Certain Poisons and Antiseptics.

With the view of comparing the oxidase of the potato with other known enzymes in its conduct towards certain poisons, it occurred to us to try the effect of a number of well-known antiseptics on active extracts of the potato. The following antiseptics were employed in the investigation of this phase of the problem: Silver nitrate, mercuric chloride, hydrocyanic acid, hydroxylamine, sulphurous acid, acid sodium sulphite, sodium thiosulphate, caustic soda, ammonia, phenylhydrazine, and hydrochloric, hydrobromic, nitrotoluenesulphonic, oxalic, and salicylic acids.

Series I.—Two cc. of fresh potato extract and 1 cc. of water or antiseptic solution were used in each experiment. The tubes were allowed to stand two minutes after adding the antiseptic before guaiacum was added. Then 0.1 cc. of fresh tincture of guaiacum was added. The following are the results:

Substance used.	Effect produced by guaiacum.
Water	Dark-blue
Potassium chloride, N/10	"
Salicylic acid, N/10	As blue as the experiment with water at first, then bleached
Silver nitrate, N/10	Dark-blue
Mercuric chloride, N/10	"
Hydrocyanic acid, N/10	No blue color developed, but remained yellow

When 1 cc. of N/10 silver nitrate was mixed with 2 cc. of the active potato extract, and the mixture allowed to stand for fifteen minutes, no blue color was produced on adding guaiacum. On standing for ten minutes, however, a blue color developed which ultimately became as deep in tint as that obtained with the extract alone.

In still a third experiment with silver nitrate, an active potato extract and a 10 per cent silver nitrate solution were mixed in equal volumes. The coagulum produced was filtered off and the clear filtrate treated with guaiacum. A beautiful blue color was obtained.[1]

It will be seen that of the substances tried in this series, only hydrocyanic and salicylic acid inhibited the bluing of the guaiacum by the potato extract.

Series II. With N/10 acids.—Two cc. of fresh potato extract and 1 cc. of water, or the solutions of N/10 acids, were employed in these experiments. The acid was allowed to remain in contact with the potato extract one minute before adding the guaiacum. The following are the results:

Substance.	Effect of guaiacum.
Water	Dark-blue
Nitrotoluenesulphonic acid	Dark-blue at first. Then bleached in the order named
Benzenesulphonic “	
Hydrochloric “	
Hydrobromic “	
Salicylic “	
Oxalic “	

A second series with the same acids, under the same conditions as in the preceding, except that the acids were allowed to remain in contact with the potato extract five minutes before adding the guaiacum, gave the following results:

Substance used.	Effect of guaiacum.
Water	Dark-blue
Nitrotoluenesulphonic acid	No blue color developed
Benzenesulphonic “	
Hydrochloric “	
Hydrobromic “	
Oxalic “	
Salicylic “	Light-blue, soon bleaching out.

Series III. With hydrocyanic acid.—In 1867, Schönbein studied the remarkable effects of hydrocyanic acid on the oxidizing ferments, and showed that very small amounts of this acid serve to inhibit all these processes of oxidation, and in many instances stop them altogether. It seemed of interest to repeat these experiments in this connection, using hydrocyanic acid of known strength. Two cc. of fresh potato extracts were employed, together with varying amounts of hydrocyanic acid of different strengths. The acid remained in contact with the potato extract one minute before adding the guaiacum. The results are as follows:

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[1] Some time after these experiments with silver nitrate and mercuric chloride were first tried, it was found that both of these substances oxidized guaiacum slowly. The fact that these poisons exert practically no effect on the oxidizing substance of the potato, was proved by comparing solutions of potato extract and these salts with their aqueous solutions of the same strength, in their power to produce guaiacum-blue. In every case the solutions containing fresh potato extract gave the guaiacum-blue at once, whereas the aqueous solutions gave it only after long standing.

Substance used.	Effect of guaiacum.
1.0 cc. of water	Dark-blue
0.9 " " " and 0.1 cc. normal HCN	No blue color developed
0.95 cc. of water and 0.05 cc. normal HCN	Very slight blue color
0.99 cc. of water and 0.01 cc. normal HCN	Very light-blue

In these experiments, an excess of guaiacum failed to intensify the color produced by the 0.1 cc. of guaiacum originally added. Three per cent hydrogen peroxide, however, intensified the blue colors produced in the tubes containing 0.05 and 0.01 cc. of the normal acid.[1] It was further observed that hydrocyanic acid fails to destroy guaiacum-blue when once it is formed. One-tenth of a cubic centimeter of normal acid also failed to prevent the formation of guaiacum-blue when hydrogen peroxide was originally present in the fresh potato extract.

A second series with normal hydrocyanic acid was tried, allowing the acid to remain in contact with the potato extract five minutes before adding the guaiacum, with the following results:

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[1] In view of the effect of hydrogen peroxide on extracts whose power to turn guaiacum blue has been destroyed by hydrocyanic acid, the use of hydrogen peroxide as an antidote for hydrocyanic acid poisoning, as recently suggested by Herting, is exceedingly interesting (Ztschr. angew. Chem., 1901, p. 585). If this has not already been tried on the animal, it would seem likely, however, that the production of gas emboli might defeat its purpose.

Substance used.	Effect of guaiacum.
1.0 cc. water	Dark-blue
0.99 " " and 0.01 cc. normal HCN	No blue color developed in any of these tubes
0.95 " " " 0.05 " " "	
0.9 " " " 0.1 " " "	
0.5 " " " 0.5 " " "	
0.0 " " " 1.0 " " "	

With N/100 hydrocyanic acid the following results were obtained after allowing the acid to remain in contact with the potato extract for five minutes:

Quantities of N/100 HCN and water used.	Effect of guaiacum.
1.0 cc. water	Dark-blue
0.9 " " and 0.1 cc. N/100 HCN	Very light-blue
0.95 " " " 0.05 " " "	Light-blue
0.99 " " " 0.01 " " "	"

With even the smallest amount of N/100 acid employed there was a marked retardation in the development of the blue color with guaiacum. This quantity, 9 parts in 10,000,000, very nearly marks the limit of the poisonous effect of the acid on the oxidizing substance in the potato.

Series IV. With hydroxylamine.—Hydroxylamine was the next substance tried. This base was prepared by dissolving a weighed amount of the hydrochloride in the desired amount of water and adding the calculated quantity of caustic soda. In our first series of experiments we used N/10 hydroxylamine, and 2 cc. of potato extract. One-tenth cc. of guaiacum was added immediately after the addition of the hydroxylamine.

Volume of water and N/10 hydroxylamine used.	Effect of guaiacum.
1.0 cc. water and 0.0 cc. hydroxylamine	Dark-blue
0.5 " " " 0.5 " "	No blue color developed
0.9 " " " 0.1 " "	
0.95 " " " 0.05 " "	
0.98 " " " 0.02 " "	Very light-blue

Volume of water and N/100 hydroxylamine used.	Effect of guaiacum.
1.0 cc. water and 0.0 cc. hydroxylamine	Dark-blue
0.5 " " " 0.5 " "	No blue color developed
0.9 " " " 0.1 " "	Very light-blue
0.95 " " " 0.05 " "	

Volume of water and N/1000 hydroxylamine used.	Effect of guaiacum.
1.0 cc. water and 0.0 cc. hydroxylamine	Dark-blue
0.5 " " " 0.5 " "	Trace of blue
0.9 " " " 0.1 " "	Light-blue
0.95 " " " 0.5 " "	

Series V. With phenylhydrazine (free base).—Preliminary experiments with phenylhydrazine showed that it acted so powerfully that it was decided to employ this substance in N/100 solution in making the tests. Tubes were prepared in the usual manner containing 2 cc. of fresh potato extract. To this quantity of potato extract, water and the solution of phenylhydrazine were added in amounts given below, and 0.1 cc. of tincture of guaiacum was added immediately thereafter. The following results were obtained :

Volume of water and N/100 phenylhydrazine used.	Effect of guaiacum.
1.0 cc. water and 0.0 cc. phenylhydrazine	Dark-blue
0.5 " " " 0.5 " "	No blue color developed
0.9 " " " 0.1 " "	
0.95 " " " 0.05 " "	

Even an excess of guaiacum failed to bring out any blue color in any of the tubes containing N/100 phenylhydrazine. An excess of 3 per cent hydrogen peroxide produced blue with 0.1 and 0.05 cc. of N/100 phenylhydrazine, but not with 0.5 cc. of this solution.

Series VI. With N/1000 phenylhydrazine (free base).—The conditions were the same as in the preceding series with N/100 solution.

Volume of water and N/1000 phenylhydrazine used.	Effect of guaiacum.
1.0 cc. of water and 0.0 cc. of N/1000 phenylhydrazine	Dark-blue
0.5 cc. of water and 0.5 cc. of N/1000 phenylhydrazine	No blue color developed
0.9 cc. of water and 0.1 cc. of N/1000 phenylhydrazine	Blue (lighter than with water alone)
0.95 cc. of water and 0.05 cc. of N/1000 phenylhydrazine	Blue (lighter than with water alone)

The tube containing 0.5 cc. N/1000 phenylhydrazine gave no color even with an excess of guaiacum. On adding 3 per cent hydrogen peroxide, however, it became blue. About 0.1 cc. N/1000 phenylhydrazine probably represents the limit of the action of this base on active potato extracts. Under the conditions of the experiment, this corresponds to 3.6 parts per million.[1]

Essentially similar results were obtained with phenylhydrazine hydrochloride. Three and six-tenths parts of this salt per million were found slightly to inhibit the oxidizing power of the fresh potato extract towards guaiacum.

Action of Sodium Thiosulphate on Active Potato Extracts.

The effect of sodium thiosulphate on active potato extracts was tried with the following results. In all of our experiments with this substance 2 cc. of an active potato extract was employed. This was always diluted to 3 cc. with water, or sodium thiosulphate, or both. In the first two series of experiments the guaiacum was added immediately.

Volume of water and N/100 thiosulphate used.	Effect of guaiacum.
1.0 cc. of water and 0.0 cc. of thiosulphate	Dark-blue
0.5 cc. of water and 0.5 cc. of thiosulphate	No blue color produced
0.9 cc. of water and 0.1 cc. of thiosulphate	Very faint-blue color
0.95 cc. of water and 0.05 cc. of thiosulphate	Faint-blue color

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[1] On account of the similarity between hydrocyanic acid and phenylhydrazine in their conduct towards the oxidizing substance of the potato, it occurred to us that the latter ought to prove a respiratory poison like the former. It has long been known that phenylhydrazine is a dangerous poison. In order to form a better idea of its action and to determine the lethal dose, its effect was tried on a kitten weighing 515 grams. A solution of phenylhydrazine was prepared containing 0.01324 gram or 0.2 grains per cc. One cc. of this solution was injected into the kitten subcutaneously. In two or three minutes the kitten was prostrated, and from this time on until death, which occurred twenty-six minutes after the injection, respiration was feeble and irregular. The heart continued to beat feebly for three minutes after respiration had ceased. The only noteworthy post-mortem condition was the chocolate color of the blood, due doubtless to the formation of methæmoglobin.

Volume of water and N/1000 thiosulphate used.	Effect of guaiacum.
1.0 cc. of water and 0.0 cc. of thiosulphate	Dark-blue
0.5 cc. of water and 0.5 cc. of thiosulphate	Faint-blue
0.9 cc. of water and 0.1 cc. of thiosulphate	Dark-blue
0.95 cc. of water and 0.05 cc. of thiosulphate	"

Similar experiments were tried with N/1000 sodium thiosulphate, allowing the tubes to stand for five minutes before adding the guaiacum. The results were precisely like those obtained with N/1000 sodium thiosulphate by adding the guaiacum instantly.

It will be seen from these results that sodium thiosulphate reacts almost as powerfully on active extracts of the potato as phenylhydrazine, and yet sodium thiosulphate does not act as a poison towards most enzymes. The fact, therefore, that it acts so injuriously on the oxidizing substance of the potato, while silver nitrate and mercuric chloride do not would seem to indicate that the oxidizing substance of the potato is not a true ferment.

Conduct of Peroxides Toward Antiseptics.

In view of the close analogy existing between certain of the peroxides and the oxidizing substance in the potato, it was thought advisable to test the conduct of these substances toward those antiseptics that were observed to be most injurious to the oxidizing power of the potato extracts.

Benzoyl peroxide was the first of these substances tested in this way, the mode of procedure being as follows :

Small amounts of benzoyl peroxide were placed in test-tubes and the antiseptic to be tested was added in known amount. After standing for a certain time, 0.1 cc. of tincture of guaiacum was added and the color noted. Hydrocyanic acid was the first substance tried. On adding 1 cc. of normal acid to a small amount of benzoyl peroxide and allowing the acid to remain in contact with it for fifteen minutes, and then adding guaiacum, a light-blue color was slowly developed. By comparing this with the action of benzoyl peroxide in water on guaiacum, it was observed that a very marked retardation in the bluing of the guaiacum had been effected by the hydrocyanic acid. In the same way it was observed that, while a small amount of benzoyl peroxide in 1 cc. of water speedily developed a deep-blue color with guaiacum, the same amount of peroxide failed to give a blue color with guaiacum when mixed with 1 cc. of N/10 *p*-nitrotoluenesulphonic acid, and allowed to stand three minutes.

This led us to try the action of some of these substances on a solution of benzoyl peroxide. This was obtained by boiling a small solution of benzoyl peroxide with water, filtering, and cooling the filtrate. Under these circumstances a very small amount of the peroxide remains in solution. With guaiacum alone, such solutions give a splendid blue color. In the following experiments 2 cc. of the solution were used with 1 cc. of the antiseptic. The latter was allowed to remain in contact with the peroxide two minutes before adding the guaiacum. The following are the results:

Substances used.	Effect of guaiacum.
N/10 *p*-Nitrotoluenesulphonic acid	No blue color developed
Normal hydrocyanic acid	Slight blue color which soon faded
N/10 Hydrochloric "	Slight blue color which soon faded
N/10 Hydrobromic "	Same results as with N/10 HCl

In a second series of experiments the acids were allowed to act on the solution of benzoyl peroxide for fifteen minutes before adding the guaiacum. Other conditions were the same as in the preceding series. The results are as follows:

Substances used.	Effect of guaiacum.
N/10 *p*-Nitrotoluenesulphonic acid	Very slight blue color at first, soon bleached
Normal hydrocyanic acid	No blue color developed except after long standing, then only faint-blue

Substances used.	Effect of guaiacum.
N/10 Benzenesulphonic acid	Light-blue, soon bleached
N/10 Hydrochloric "	Same as with benzenesulphonic acid
N/10 Oxalic "	Same as with hydrochloric acid only bleached more slowly

Benzoyl Peroxide and Phenylhydrazine.

Tubes were prepared containing 2 cc. of a saturated solution of benzoyl peroxide. With 0.1 cc. of guaiacum, this solution gave a splendid blue color. The action of phenylhydrazine on these portions of benzoyl peroxide was tried at the following dilutions, and in quantities indicated below. The results are as follows :

Substances used.	Effect of guaiacum.
0.9 cc. of water and 0.1 cc. of N/100 phenylhydrazine	Only the faintest blue color
0.95 cc. of water and 0.05 cc. of N/10 phenylhydrazine	Very light-blue
0.99 cc. of water and 0.01 cc. of N/100 phenylhydrazine	Much lighter blue than with 1.0 cc. of water alone
0.9 cc. of water and 0.1 cc. of N/1000 phenylhydrazine	All of these showed a marked falling off in color, in the order named, as compared with that produced in the presence of 1.0 cc. of water alone
0.95 cc. of water and 0.05 cc. of N/1000 phenylhydrazine	
0.99 cc. of water and 0.01 cc. of N/1000 phenylhydrazine	

It will be observed, therefore, that even 3.6 parts of phenylhydrazine in 10,000,000 inhibit the action of benzoyl peroxide on guaiacum.

Benzoyl Peroxide and Hydroxylamine.

In order to test the effect of hydroxylamine on benzoyl peroxide, tubes were prepared containing 2 cc. of a saturated solution of the latter. A N/10 solution of hydroxylamine was used in quantities indicated in the following. One-tenth cc. guaiacum was added at once after the addition of the hydroxylamine. The following are the results :

Substances used.	Effect of guaiacum.
1.0 cc. of water and 0.0 cc. of hydroxylamine	Dark-blue
0.5 cc. of water and 0.5 cc. of hydroxylamine	No blue color developed
0.9 cc. of water and 0.1 cc. of hydroxylamine	Very pale-blue
0.95 cc. of water and 0.05 cc. of hydroxylamine	Light-blue

Precisely similar results were reached in a second series of experiments, in which the same quantities of hydroxylamine were allowed to act on the peroxide for five minutes before adding the guaiacum.

It has been pointed out above that certain metallic peroxides and oxides produce guaiacum-blue with fresh tinctures of guaiacum. It has also been observed, in this connection, that their action on guaiacum is inhibited by the same antiseptics and poisons that prevent the production of guaiacum-blue by organic peroxides and fresh potato extracts. That this is the case may be seen from the following results:

Effect of Phenylhydrazine on the Production of Guaiacum-Blue by Lead Peroxide.

Tubes were prepared containing small amounts of lead peroxide and 2 cc. of water. To these, small amounts of phenylhydrazine were added. The tubes were then allowed to stand a few moments, when 0.1 cc. of tincture of guaiacum was added to each tube. The following results were obtained:

Substances used.	Effect of guaiacum.
1.0 cc. of water and 0.0 cc. of N/100 phenylhydrazine	Dark-blue
0.5 cc. of water and 0.5 cc. of N/100 phenylhydrazine	No blue color developed
0.9 cc. of water and 0.1 cc. of N/100 phenylhydrazine	" " " "
0.95 cc. of water and 0.05 cc. of N/100 phenylhydrazine	" " " "

It will be observed, therefore, that 18 parts of phenylhydrazine per 1,000,000 is sufficient to prevent the production of guaiacum-blue by means of lead peroxide.

The effect of N/100 phenylhydrazine was tried on a second sample of lead peroxide in exactly the manner described above. With water and guaiacum alone this sample of lead peroxide gave a splendid blue color. With 0.5 cc. N/100 phenylhydrazine no blue color was obtained, even after standing, whereas very faint-blue tints were ultimately obtained by adding guaiacum to the tubes containing 0.1 cc. and 0.05 cc. N/100 phenylhydrazine. These experiments were repeated three times on this sample of peroxide with like result.

The effect of N/100 phenylhydrazine on manganese dioxide and silver oxide is not quite so marked as it is on lead peroxide. The experiments were carried out exactly as with lead peroxide.

With 3 cc. water alone, silver oxide gave a dark-blue color with guaiacum.

With 0.5 cc. N/100 phenylhydrazine and 2.5 cc. of water, it gave no color with guaiacum.

With 0.1 and 0.05 cc. N/100 phenylhydrazine, and 2.9 and 2.95 cc. of water, respectively, silver oxide gave a blue color with guaiacum in each case, although not as dark a tint as that obtained with water alone.

Very small amounts of N/100 phenylhydrazine—0.1 and 0.05 cc. with 2.9 and 2.95 cc. of water, seemed to increase the power of manganese dioxide to oxidize guaiacum. On the other hand, manganese dioxide with 0.5 cc. N/100 phenylhydrazine, and 2.5 cc. of water showed only a pale-greenish tint on standing for some time after the addition of guaiacum.

With N/10 phenylhydrazine, it was found that 0.5, 0.1, and 0.05 cc. of the base absolutely prevented the production of guaiacum-blue by silver oxide and manganese dioxide (native).

Hydrocyanic acid also has the power of preventing the formation of guaiacum-blue by silver oxide and lead peroxide, as will be seen from the following experiments:

(1) With 3 cc. of water and a small amount of lead peroxide, guaiacum gave a bright-blue color.

(2) With 2.5 cc. of water and 0.5 cc. of normal hydrocyanic

acid, and the same amount of lead peroxide as in (1), guaiacum gave no blue color.

(3) Same as (2), but with 2.9 cc. of water and 0.1 cc. of normal hydrocyanic acid, guaiacum gave no blue color.

(4) Same as (2) and (3), but with 2.95 cc. of water and 0.05 cc. of normal hydrocyanic acid, no blue color with guaiacum.

With silver oxide similar experiments were tried. With 3 cc. water alone, silver oxide gave a dark-blue coloration with guaiacum. On the other hand, with 0.5, 0.1, and 0.05 cc. of normal hydrocyanic acid, and enough water in each case to make up to 3 cc., no blue color was obtained on adding 0.1 cc. guaiacum.

With 0.5, 0.1, and 0.05 cc. of N/10 hydrocyanic acid, but with the other conditions the same as in the preceding experiments, silver oxide gave no blue color with guaiacum.

Even N/100 hydrocyanic acid was found greatly to inhibit the guaiacum reaction with silver oxide. With 0.5 cc. N/100 acid and 2.5 cc. water, no blue color was developed even on standing, while with 0.1 and 0.05 cc. of N/100 acid, a light-blue color was developed some little time after adding the guaiacum. Even these showed a retardation in the development of the blue color as compared with water. It will be seen, therefore, that even 45 parts of hydrocyanic acid in 10,000,000 parts of water inhibit the oxidation of guaiacum by silver oxide. On the other hand, N/100 acid seemed to exert no effect on the bluing of guaiacum by lead peroxide. If it exerted any influence at all, it was slightly to accelerate the bluing of the guaiacum by lead peroxide, at least, in the proportion of 0.5 an 0.1 cc. of N/100 acid, with 2.5 and 2.9 cc. of water.

The effect of normal hydrocyanic acid on the power of manganese dioxide to turn guaiacum blue was also tried under conditions identical with those under which its effect on lead peroxide was studied. It was found that even normal hydrocyanic acid or an acid of 2.7 per cent, accelerated the bluing of guaiacum by manganese dioxide, both native and precipitated.

It will doubtless be gathered, from these experiments, that while there are slight differences in their mode of action, there are many fundamental resemblances between the general conduct of the oxidizing ferment of the potato and that of certain of the peroxides, organic and inorganic, towards antiseptics. We have reached the conclusion, therefore, that the oxidizing ferment, which causes the bluing of guaiacum directly, and which oxidizes phenolphthalin, etc., is in all probability nothing more than an organic peroxide,[1] which has been produced at the moment of exposure to the air, from one or more of the readily oxidizable substances contained in the cell. This view regarding oxidation phenomena in the plant is in harmony with modern conceptions concerning autoxidation in general, and at the same time it does away with the necessity for such assumptions as those of Lindet,[2] who, in order to explain why a bruised apple turns brown, although it remains white if intact, found it necessary to assume that the oxidizing ferment and the tannin (the substance oxidized) were situated in different cells, and, therefore, were brought together only by rupture of the tissues. According to the view just advocated, the so-called oxidase (peroxide), is not present at all in the intact cell, but only its forerunner, an autoxidizable substance, which, when it comes in contact with the air, by the tissue being bruised, unites with the oxygen to produce the peroxide, or the so-called oxidizing ferment. This then effects the oxidation of other reducible substances, among them tannin, which very probably are to be found in the same cell with it.

The oxidizing substance of the potato is by no means confined to the tuber of this plant, but seems to be widely distributed in the vegetable kingdom. Schönbein, in 1867, showed that the filtered extracts of a number of plants gave the guaiacum reaction, and since then these observations have been considerably extended by other investigators in this field.

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[1] As the result of his studies on "The Function of Peroxides in Phenomena of Slow Oxidation," Bach has reached similar conclusions respecting the oxidizing ferments of the blood. These, according to Bach, are simply readily oxidizable substances with a special aptitude for forming peroxides.—Compt. rend., **124**, 951 (1897).

[2] *Ibid.*, **120**, 370 (1895).

Recently Kastle and Shedd[1] have found the same, or at least a similar oxidizing substance to that in the potato, in at least a dozen different vegetable sources. Up to this time we have not been able to isolate the oxidizing substance in pure condition. It has been found to be very soluble in water, and even on the addition of alcohol only a slight turbidity results on standing, and no filterable product is obtained. Nothing, therefore, is known regarding its composition or nature beyond that already set forth above. From what has already been observed respecting its conduct, it is believed, however, that benzaldehyde may be looked upon as the prototype of the substance in the plant which on exposure to air forms the oxidizing substance, and that in the oxidation and carrying of oxygen by benzaldehyde, we have an exact analogy to the oxidation processes occurring in the plant. Baeyer and Villiger[2] have shown that when benzaldehyde is oxidized by atmospheric oxygen, benzoyl hydrogen peroxide is produced:

$$C_6H_5CHO + O_2 = C_6H_5CO.O.OH.$$

A mixture of benzaldehyde and water, shaken with air, turns guaiacum blue directly.

When benzoyl hydrogen peroxide is left in contact with water it forms benzoic acid and hydrogen peroxide:

$$C_6H_5CO.O.OH + H_2O = C_6H_5COOH + H_2O_2.$$

Or, it may oxidize a second molecule of the benzoic aldehyde so as to produce two molecules of benzoic acid:

$$C_6H_5CO.O.OH + C_6H_5CHO = 2C_6H_5COOH.$$

Or, if another reducing agent, such as indigo, which is more easily oxidized by the benzoyl hydrogen peroxide than benzaldehyde, is at hand, it oxidizes this and forms at the same time one molecule of benzoic acid, thus:

$$C_6H_5CO.O.OH + \text{indigo} = C_6H_5COOH + \text{oxidation product of indigo.}$$

In all of these reactions the point of chief interest is that while benzaldehyde can act as a carrier of oxygen, it can carry only a limited quantity, that is, one atom per molecule, and is itself oxidized to benzoic acid at the same time. In other words, while a carrier, it is not a true catalytic agent in the sense of being able to react again and again with respect to oxygen. This, of course, is for the reason that the carrier itself is oxidized to a substance which does not combine directly with atmospheric oxygen. The same seems to be true of the substance forming the peroxide in the plant. It readily unites with oxygen to form an unstable oxidizing substance, probably a peroxide, and this readily gives up its oxygen to reducing substances, such as guaiacum, phenolphthalin, tannin, etc. It can oxidize only a limited quantity of these substances, however, even in a current of air,[1] and, on standing, active potato extracts soon lose their power to turn guaiacum blue, doubtless for the reason that the oxidizing substance gives up its oxygen to reducing substances present, such as tannin, etc. That such extracts are not capable of carrying a very large quantity of oxygen is probably to be explained by the fact that the original carrier gives up only half of its oxygen to the reducing substances, and at the same time it is itself oxidized to some product which is incapable of taking up further amounts of oxygen, in just the same way that benzaldehyde is always ultimately oxidized to benzoic acid, by half the oxygen which it originally takes up from the air.

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[1] *Loc. cit.*

[2] Ber. d. chem. Ges., 33, 1569 (1900).

As to the nature of the substance in the plant which produces the oxidizing substance on exposure to oxygen, nothing definite can be said at present. It may possibly be an aldehyde. In fact Curtius and Reinke[1] have obtained from the leaves of certain green plants, by distillation in a current of steam, a di- or tetrahydro aromatic aldehyde-alcohol, to which they assigned the formula

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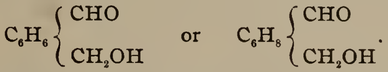
[1] See the work of Kastle and Shedd upon this point (*Loc. cit.*). In order to determine whether air would restore the activity of potato extracts that had lost their activity, two tubes were taken containing the same amounts of such an extract. Through one of these a current of air was passed for sixty-five minutes, while the other was left in an open tube during this time. On adding guaiacum to the two extracts it was found that the one through which the current of air had passed gave a little deeper blue color than the one which had stood quietly during the time. In all of our experiments in this direction, and they have been repeated several times, we have never succeeded in restoring to these exhausted extracts anything approaching their original activity, and the fact that there is any increase in activity at all may be explained by the supposition that a small amount of the original oxygen carrier may, on first exposure to the air, escape oxidation. On exposing mixtures of benzaldehyde and water to the air, for example, not all of the benzoic aldehyde is oxidized at once but only gradually.



$$C_6H_6\begin{cases}CHO\\CH_2OH\end{cases} \quad \text{or} \quad C_6H_8\begin{cases}CHO\\CH_2OH\end{cases}.$$

Such a substance would probably conduct itself towards guaiacum, etc., in much the same manner as an active potato extract. It is interesting to note, in this connection, that those antiseptics which inhibit the action of potato extracts on guaiacum to the greatest extent are those which most readily combine with aldehydes. On the other hand, it should also be noted that these same substances have proved to be the most powerful in preventing the action of peroxides upon guaiacum. Hence it may be that their power to prevent the production of guaiacum-blue may be due partly to their reducing action and partly to their power to combine with aldehydes.

The Rôle of Oxygen Carriers in the Normal Oxidation Process in the Plant.

It will be observed that we obtain evidence of these oxidizing substances in the plant only by the destruction and rupture of plant tissues, and their free exposure to air. It is pertinent, therefore, to inquire whether these carriers are concerned in the normal oxidation phenomena of the living cell. There is certainly nothing known that indicates that they are not thus concerned, nor is there anything to show that the carrier itself is produced by rupture of the cell and exposure to the air. It would seem, rather, to be a constant product of metabolic activity, and the fact that it so readily combines with oxygen on exposure to air, seems to indicate that it would also combine directly with any oxygen entering the living cell, and thereby participate in the respiratory activities of the plant. The fact that such an oxygen carrier may be present in the cell and yet not render the vegetable tissue brown in color, as always occurs when such tissue is bruised and freely exposed to the air, is capable of several explanations. It may be, for example, that with the amount of oxygen normally supplied to the tissue only such small amounts of peroxide are produced that the amount of tannin, and other substances oxidized, is imperceptible so far as their color is concerned ; or it may also be that with small amounts of the peroxide present in the tissue at any one time, other more powerful reducing agents appropriate the oxygen of the peroxide as fast as it is formed, and that the tannins therefore escape oxidation altogether. It is also to be observed, in this connection, that the accumulation of the oxygen carrier in the cell, or in any particular tissue, does not necessarily indicate an excessive oxidation for that particular cell or part. Indeed it would seem to indicate the reverse, for in the tissues of warm-blooded animals we do not find any substance capable of turning guaiacum blue directly, whereas in the potato tuber we do. Yet the failure on the part of animal tissues to give guaiacum-blue directly may not be due to the absence of the peroxide substance, but to the presence of substances more readily oxidized by the peroxide than guaiacum.

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[1] Ber. d. bot. Ges., 15, 201, 10, 26/3.

The Hydrogen Peroxide-Guaiacum Reaction.

There is still another reaction which presents a close similarity to the one under consideration, and about which it seems necessary to say a few words in this connection. That is the reaction which results in the formation of guaiacum-blue directly from tincture of guaiacum and hydrogen peroxide by animal and plant extracts, and which modern biochemists have ascribed to the enzyme called peroxidase. The power of producing guaiacum blue from a mixture of hydrogen peroxide and tincture of guaiacum is certainly a very general property of active animal and plant tissues, much more so, indeed, than the power of these tissues to give guaiacum-blue without the addition of hydrogen peroxide. It has been observed in this connection, for example, that potato extracts which had lost their power to turn guaiacum-blue directly still gave guaiacum-blue on the addition of hydrogen peroxide, either before or after the addition of tincture of guaiacum ; and in the same way a good many animal and plant tissues and secretions which do not give the guaiacum reaction directly, such as blood, liver, etc., readily give it on the addition of hydrogen peroxide. In spite of its wide distribution, however, it is not universally characteristic of living tissues. For example, the onion bulb not only does not give the guaiacum reaction directly, but it does not give it on the addition of hydrogen peroxide. It should be borne in mind, however, as Hunger has recently shown,[1] that this reaction with guaiacum and hydrogen peroxide is sometimes masked by the presence of glucose and other powerful reducing substances in the plant. The fact that hydrogen peroxide does not give the guaiacum reaction directly, or at least but faintly when heated, whereas other peroxides, especially the organic peroxides, do so, would seem to indicate that the function of the hydrogen peroxide in the guaiacum-hydrogen peroxide reaction, is to react with some one or more of the organic substances present in the plant or animal extract to form an organic peroxide. A reaction of this character has been described by Baeyer and Villiger, who have shown that acetic peroxide, one of the most unstable of these derivatives, can be readily prepared by the action of hydrogen peroxide on acetic anhydride. In fact it has been observed in this connection that hydrogen peroxide may react even with the organic acids to form organic peroxides. At least, certain of these, such as benzoic and succinic acids, have been found to give the guaiacum reaction with hydrogen peroxide.

In view of all that has been set forth above, it is believed that the action of hydrogen peroxide in the guaiacum-hydrogen peroxide reaction is much the same as that of free oxygen in the reaction in which the guaiacum-blue is produced directly by the action of the plant extract. We have seen that the latter process can be explained by the formation of an organic peroxide from the oxygen of the air and some readily autoxidizable substance contained in the extract. It would seem probable, therefore, that the action of the hydrogen peroxide on the extract is to convert some organic compound, which would not be acted on in this way by molecular oxygen, into a peroxide.

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[1] Ber. d. bot. Ges., 19, 374.

On the other hand, it is possible that the peroxidase may react in such a manner as to weaken the bonds of the oxygen in the hydrogen peroxide, somewhat after the manner of the catalase described by Loew[1] and others, whereby it becomes able to oxidize the guaiacum. The fact that hydrogen peroxide turns guaiacum faintly blue when heated, and that its powers of oxidation are generally greatly increased by oxygen carriers such as ferrous and ferric salts, would seem to indicate the possibility of such an action on the part of the animal or plant extract. It is our intention to investigate the power of such extracts to act as oxygen carriers in the presence of hydrogen peroxide, particularly in such reactions as the oxidation of formaldehyde and phenolphthalin by hydrogen peroxide. In fact, studies with this end in view have already been begun in this laboratory.

In conclusion, it may be said that the results reached in the present investigation seem to warrant the following conclusions:

1. That oxygen is absolutely essential to the production of the guaiacum-bluing ferment of the potato.

2. That this so-called oxidizing ferment is in all probability not a true soluble ferment, but an organic peroxide.

3. That the oxidation phenomena occurring in the plant, and probably in the animal organism also, can be satisfactorily explained upon the supposition that the readily autoxidizable substances which they contain are oxidized to the peroxide condition by molecular oxygen, and that the peroxides thus formed in turn give up part of their oxygen to other less oxidizable substances present in the cell. In other words, that the process of rendering oxygen active, by the living cell, is probably brought about in essentially the same way that this is accomplished by phosphorus, benzaldehyde and other oxygen carriers, *viz.*, as one phase of autoxidation.

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[1] U. S. Dept. of Agr., Report 68.

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$C_{10}H_{12}O_2$. Secondary butyl benzoate. *J. F. Norris* and *E. H. Green* 312

10 III.

$C_{10}H_{13}O_2N_3$. Ethyl phenylisobiuret. *R. H. McKee* 258
Hydrochloride ; action of hydrochloric acid.
$C_{10}H_{14}ON_2$. Ethyl *o*-tolylisourea. *R. K. McKee* 234
$C_{10}H_{14}ON_2$. Ethyl methylphenylisourea. *R. H. McKee* 236
$C_{10}H_{14}ON_2$. Methyl (*asym.*)-ethylphenylisourea. *R. H. McKee* 241
$C_{10}H_{11}O_2Cl$. Ethyl phenylchloracetate. *H. L. Wheeler* 352
$C_{10}H_{15}O_6Cl$. Tricarbethoxychlormethane. *H. L. Wheeler* 351
$C_{10}H_{11}NS$. Mesityl thiocyanate. *H. L. Wheeler* and *T. B. Johnson* 205

10 IV.

$C_{10}H_{11}ONS_2$. Dimethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 193
$C_{10}H_{12}ON_2S$. Acetylphenylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412

C_{11}-GROUP.

$C_{11}H_{14}O_2$. Ethylhydrocinnamate. *H. L. Wheeler* and *T. B. Johnson* 199
Derivative of, and benzoyldithiocarbamic acid.

11 IV.

$C_{11}H_{11}O_2NS$. Ethyl phenylthiocyanacetate. *H L. Wheeler* 352
$C_{11}H_{13}ONS_2$. Methyl ethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 194

C_{12}-GROUP.

$C_{12}H_8O_2$. Phenoxozone. *H. W. Hillyer* 361
Derivatives.
$C_{12}H_8O_6$. Orthodioxyphenyloxyorthoquinone. *C. L. Jackson* and *W. Koch* 25
$C_{12}H_{22}O_4$. Disecondary butyl succinate. *J. F. Norris* and *E. H. Green* 311
$C_{12}O_4Br_6$. Hexabrom-*o*-quinopyrocatechin. *C. L. Jackson* and *W. Koch* 35

12 III.

$C_{12}H_6O_6N_2$. Dinitrophenoxozone. *H. W. Hillyer* 361
$C_{12}H_8O_7N_2$. Dioxydinitrophenoxide. *H. W. Hillyer* 366
  Sodium and silver salts.

$C_{12}H_{10}O_2N_2$. Benzene-4-azoresorcin. *W. R. Orndorff* and *E. D. Thebaud* 159
  On two modifications of, and the oxyazo compounds.

$C_{12}H_{10}O_2N_2$. Diamidophenoxozone. *H. W. Hillyer* 362
$C_{12}H_{10}O_4S$. Orthodioxydiphenylsulphone. *C. L. Jackson* and *W. Koch* 32
  (Pyrocatechinsulphone.)

12 IV.

$C_{12}H_8O_4N_3Br$. Bromanilidodinitrobenzol. *C. L. Jackson* and *W. P. Cohoe* 5
  Also *C. L. Jackson* and *R. B. Earle* 45
$C_{12}H_{13}O_3NS_2$. Ethyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 197
$C_{12}H_{15}ONS_2$. Diethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 194
$C_{12}H_{16}ON_2S$. Acetylmethylphenylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413
$C_{12}H_{24}ON_2S$. Acetyldiisobutylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 411

C_{13}-GROUP.

$C_{13}H_{12}$. Diphenylmethane. *J. F. Norris* and *G. MacLeod* 501

13 II.

$C_{13}H_6Cl_6$. 2,5,2',5'-Tetrachlorbenzophenone chloride. *J. F. Norris* and *E. H. Green* 497
$C_{13}H_8Cl_4$. 4,4'-Dichlorbenzophenone chloride. *J. F. Norris* and *E. H. Green* .. 495
$C_{13}H_{11}Cl$. Diphenylchlormethane. *J. F. Norris and G. MacLeod* 504

13 III.

$C_{13}H_{12}ON_2$. Diphenylurea. *R. H. McKee* 223
  From ethyl phenylisourea.

$C_{13}H_6OCl_4$. 2,5,2',5'-Tetrachlorbenzophenone. *J. F. Norris* and *E. H. Green* ... 498
$C_{13}H_8OCl_2$. 4,4'-Dichlorbenzophenone. *J. F. Norris* and *E. H. Green* 496
$C_{13}H_{18}OBr_2$. 4,4'-Dibrombenzophenone. *J. F. Norris* and *E. H. Green* 497

13 IV.

$C_{13}H_{15}O_3NS_2$. Ethyl propionate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 201
$C_{13}H_{17}ONS_2$. Isoamyl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 195
$C_{13}H_{25}ONS_2$. Diisoamyl acetylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 193

C_{14}-GROUP.

$C_{14}H_{10}O_4$. Benzoyl peroxide. *J. H. Kastle* and *M. E. Clarke* 522
  Action on hydrogen peroxide. See also *J. H. Kastle* and *A. S. Loevenhart* 554
  Action of hydroxylamine, phenylhydrazine, and antiseptics.

14 III.

$C_{14}H_9O_2N$. *s*-Phenylphthalimide. *M. Kuhara* and *M. Fukui* 455
Also *a*-compound.

$C_{14}H_{10}O_4N_2$. Oxyphthalylnitrosoaniline. *M. Kuhara* and *M. Fukui* 458
$C_{14}H_{11}ON_3$. Benzoylphenyleneguanidine. *H. L. Wheeler* and *T. B. Johnson* 415
$C_{14}H_{11}O_3N$. Phenylphthalamic acid. *M. Kuhara* and *M. Fukui* 457
$C_{14}H_{12}O_2N_2$. *Sym*-benzoylphenylurea. *R. H. McKee* 228
Also *as*-benzoylphenylurea.

$C_{14}H_{13}ON_3$. Benzoylphenylguanidine. *H. L. Wheeler* and *T. B. Johnson* 417
$C_{14}H_{21}O_{16}O_6$. Styphnic ethyl ether. *C. L. Jackson* and *R. B. Earle* 52
$C_{14}H_{11}NS$. Diphenylmethylisothiocyanate. *H. L. Wheeler* 353
$C_{14}H_{14}NS$. Diphenylmethylthiourea. *H. L. Wheeler* 355

14 IV.

$C_{14}H_{19}ONS_2$. Di-*n*-propylbenzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 195
$C_{14}H_{20}ON_2S$. Benzoyldiethylthioldiethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413

C_{15}-GROUP.

$C_{15}H_{16}S$. Metaxylyl benzyl sulphide. *H. L. Wheeler* and *T. L. Johnson* 205

15 III.

$C_{15}H_{11}O_2N$. Orthotolylphthalimide. *M. Kuhara* and *M. Fukui* 458
s- and *a*-compounds.

$C_{15}H_{12}O_4N_2$. Oxyphthalylnitrosoorthotoluidine. *M. Kuhara* and *M. Fukui* 459
$C_{15}H_{13}O_3N$. Orthotolylphthalamic acid. *M. Kuhara* and *M. Fukui* 459
$C_{15}H_{14}O_2N_2$. Methyl benzoylphenylisourea. *R. H. McKee* 231
Sym. and *as.*-compounds.
$C_{15}H_{15}ON$. Diphenylmethylacetamide. *H. L. Wheeler* 354
$C_{15}H_{15}O_2N_3$. Methyl (*sym.*)-diphenylisobiuret. *R. H. McKee* 233
$C_{15}H_{16}N_2S$. Diphenylmethyl-methylthiourea. *H. L. Wheeler* 355

15 IV.

$C_{15}H_{11}ONS$. Desyl thiocyanate. *H. L. Wheeler* and *T. L. Johnson* 202
$C_{15}H_{12}ON_2S$. Diphenylpseudothiolhydantoïn. *H. L. Wheeler* 353
$C_{15}H_{12}O_3N_2S_2$. Paranitrobenzylbenzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 196
$C_{15}H_{17}O_5NS_2$. Benzoylmetanitrophenylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412
$C_{15}H_{17}O_5NS_2$. Diethyl malonate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* 351

15 V.

$C_{15}H_{12}ONS_2Br$. Parabrombenzyl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 197

C_{16}-GROUP.

$C_{16}H_{10}O_2N_2$. Indigo. *H. Brunck* 387
History of manufacture (Review).

$C_{16}H_{14}O_4N_2$. Diacetyldiamidophenoxozone. *H. W. Hillyer* 364
$C_{16}H_{16}O_2N_2$. Ethyl benzoylphenylisourea. *R. H. McKee* 227
$(C_{16}H_{18}N_2O_3)x$. Bilirubin. *W. R. Orndorff* and *J. E. Teeple* 86
$C_{16}H_{22}N_2S$. Diphenylmethyl-diethylthiourea. *H. L. Wheeler* 355

7 III.

$C_7H_8ON_2$. Monophenylurea. *R. H. McKee* 218
C_7H_5OCl. Benzoyl chloride. *G. Benson* and *H. W. Hillyer* 373
Action on ammonium sulphocyanate.

7 IV.

$C_7H_7O_5NS$. Nitrotoluenesulphonic acid. *J. H. Kastle* and *A. S. Loevenhart* 549
Action on potato oxidase and benzoyl peroxide.
$C_7H_{13}ONS_2$. Diethyl acetylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 193

C_8-GROUP.

C_8H_{18}. Dimethyl-3,4-hexane. *J. F. Norris* and *E. H. Green* 313
(Disecondarybutyl.)

8 II.

$C_8H_{16}O$. Dimethylpinacoline. *J. F. Norris* and *E. H. Green* 317
(Dimethyl-3-hexanon-4.)
$C_8H_{18}O_2$. Dimethylpinacone. *J. F. Norris* and *E. H. Green* 315
(Dimethyl-3,4-hexandiol-3,4).
$C_8H_8N_2$. Methylphenylcyanamide. *R. H. McKee* 236
$C_8H_{11}N$. Monoethylaniline. *R. H. McKee* 223
From ethyl phenylisourea.
$C_8H_{10}S$. Metaxylyl mercaptan. *H. L. Wheeler* and *T. B. Johnson* 205

8 III.

$C_8H_9O_2N_3$. α-Phenylbiuret. *R. H. McKee* 254
$C_8H_{10}ON_2$. Methyl phenylisourea. *R. H. McKee* 228
Hydrochloride, sulphate, action of benzoyl chloride on.
$C_8H_4O_2Cl_2$. Phthalyl chloride. *M. Kuhara* and *M. Fukui* 454

8 IV.

$C_8H_{11}O_4NS$. Diethylthiocyanmalonate. *H. L Wheeler* 350
$C_8H_{15}ONS_2$. Isoamyl acetylimidodithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 193

C_9-GROUP.

$C_9H_{14}O_2$. Racemic campholytic acid. *W. A. Noyes* and *Wm. Blanchard* 281
Dihydro-, dihydrohydroxy-, bromdihydrocampholytic acid. Amide of campholytic acid.
$C_9H_{16}O_2$. Dihydro-α-campholytic acid. *W. A. Noyes* and *Wm. Blanchard* 288
Preparation; amide.
$C_9H_{16}O_3$. Dihydrohydroxycampholytic acid. *W. A. Noyes* and *Wm. Blanchard* 281
$C_9H_{17}O_2$. Secondary butyl isovalerianate. *J. F. Norris* and *E. H. Green* 311

9 III.

$C_9H_{10}O_2N_2$. Benzoylmethylurea. *R. H. McKee* 250
$C_9H_{11}O_2N_3$, Methyl phenylisobiuret. *R. H. McKee* 253
$C_9H_{12}ON_2$. Ethyl phenylisourea. *R. H. McKee* 214
(Ethyl phenylimidocarbamate). Preparation; action of air, water, hydrochloric acid, ammonia, aniline, and benzoyl chloride.

$C_9H_{12}ON_2$. Methyl (*asym.*)-methylphenylisourea. *R. H. McKee* 241

$C_9H_{15}O_2Br$. α-Bromdihydro-*i*-α-campholytic acid. *W. A. Noyes* and *W. M. Blanchard* 289

C_9H_9NS. Ethyl 1′-thiocyanbenzene. *H. L. Wheeler* and *T. B. Johnson* 202

C_9H_9NS. 1′.*m*-xylylthiocyanate. *H. L. Wheeler* and *T. B. Johnson* 203

9 IV.

$C_9H_{12}ONCl$. Ethyl imidobenzoate hydrochloride. *R. H. McKee* 259
Hydrolysis of.

$C_9H_{13}ON_2Cl$. Ethyl phenylisourea hydrochloride. *R. H. McKee* 216, 259
Preparation and hydrolysis.

$C_9H_7O_2NS$. Phenyl thiocyanacetate. *H. L. Wheeler* and *T. B. Johnson* 200

$C_9H_{18}ON_2S$. Acetyldiethylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413

C$_{10}$-GROUP.

$C_{10}H_{13}O_2$. Secondary butyl benzoate. *J. F. Norris* and *E. H. Green* 312

10 III.

$C_{10}H_{13}O_2N_3$. Ethyl phenylisobiuret. *R. H. McKee* 258
Hydrochloride ; action of hydrochloric acid.

$C_{10}H_{14}ON_2$. Ethyl *o*-tolylisourea. *R. K. McKee* 234

$C_{10}H_{14}ON_2$. Ethyl methylphenylisourea. *R. H. McKee* 236

$C_{10}H_{14}ON_2$. Methyl (*asym.*)-ethylphenylisourea. *R. H. McKee* 241

$C_{10}H_{11}O_2Cl$. Ethyl phenylchloracetate. *H. L. Wheeler* 352

$C_{10}H_{15}O_6Cl$. Tricarbethoxychlormethane. *H L. Wheeler* 351

$C_{10}H_{11}NS$. Mesityl thiocyanate. *H. L. Wheeler* and *T. B. Johnson* 205

10 IV.

$C_{10}H_{11}ONS_2$. Dimethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 193

$C_{10}H_{12}ON_2S$. Acetylphenylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412

C$_{11}$-GROUP.

$C_{11}H_{14}O_2$. Ethylhydrocinnamate. *H. L. Wheeler* and *T. B. Johnson* 199
Derivative of, and benzoyldithiocarbamic acid.

11 IV.

$C_{11}H_{11}O_2NS$. Ethyl phenylthiocyanacetate. *H L. Wheeler* 352

$C_{11}H_{13}ONS_2$. Methyl ethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 194

C$_{12}$-GROUP.

$C_{12}H_8O_2$. Phenoxozone. *H. W. Hillyer* 361
Derivatives.

$C_{12}H_8O_5$. Orthodioxyphenyloxyorthoquinone. *C. L. Jackson* and *W. Koch* 25

$C_{12}H_{22}O_4$. Disecondary butyl succinate. *J. F. Norris* and *E. H. Green* 311

$C_{12}O_4Br_6$. Hexabrom-*o*-quinopyrocatechin. *C. L. Jackson* and *W. Koch* 35

12 III.

$C_{12}H_6O_6N_2$. Dinitrophenoxozone. *H. W. Hillyer* ... 361

$C_{12}H_8O_7N_2$. Dioxydinitrophenoxide. *H. W. Hillyer* ... 366
Sodium and silver salts.

$C_{12}H_{10}O_2N_2$. Benzene-4-azoresorcin. *W. R. Orndorff* and *E. D. Thebaud* ... 159
On two modifications of, and the oxyazo compounds.

$C_{12}H_{10}O_2N_2$. Diamidophenoxozone. *H. W. Hillyer* ... 362

$C_{12}H_{10}O_4S$. Orthodioxydiphenylsulphone. *C. L. Jackson* and *W. Koch* ... 32
(Pyrocatechinsulphone.)

12 IV.

$C_{12}H_8O_4N_3Br$. Bromanilidodinitrobenzol. *C. L. Jackson* and *W. P. Cohoe* ... 5
Also *C. L. Jackson* and *R. B. Earle* ... 45

$C_{12}H_{13}O_3NS_2$. Ethyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* ... 197

$C_{12}H_{15}ONS_2$. Diethyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* ... 194

$C_{12}H_{16}ON_2S$. Acetylmethylphenylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* ... 413

$C_{12}H_{24}ON_2S$. Acetyldiisobutylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* ... 411

C_{13}-GROUP.

$C_{13}H_{12}$. Diphenylmethane. *J. F. Norris* and *G. MacLeod* ... 501

13 II.

$C_{13}H_6Cl_6$. 2,5,2',5'-Tetrachlorbenzophenone chloride. *J. F. Norris* and *E. H. Green* ... 497

$C_{13}H_8Cl_4$. 4,4'-Dichlorbenzophenone chloride. *J. F. Norris* and *E. H. Green* ... 495

$C_{13}H_{11}Cl$. Diphenylchlormethane. *J. F. Norris and G. MacLeod* ... 504

13 III.

$C_{13}H_{12}ON_2$. Diphenylurea. *R. H. McKee* ... 223
From ethyl phenylisourea.

$C_{13}H_6OCl_4$. 2,5,2',5'-Tetrachlorbenzophenone. *J. F. Norris* and *E. H. Green* ... 498

$C_{13}H_8OCl_2$. 4,4'-Dichlorbenzophenone. *J. F. Norris* and *E. H. Green* ... 496

$C_{13}H_{18}OBr_2$. 4,4'-Dibrombenzophenone. *J. F. Norris* and *E. H. Green* ... 497

13 IV.

$C_{13}H_{15}O_3NS_2$. Ethyl propionate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* ... 201

$C_{13}H_{17}ONS_2$. Isoamyl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* ... 195

$C_{13}H_{25}ONS_2$. Diisoamyl acetylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* ... 193

C_{14}-GROUP.

$C_{14}H_{10}O_4$. Benzoyl peroxide. *J. H. Kastle* and *M. E. Clarke* ... 522
Action on hydrogen peroxide. See also *J. H. Kastle* and *A. S. Loevenhart* 554
Action of hydroxylamine, phenylhydrazine, and antiseptics.

14 III.

$C_{14}H_9O_2N$. *s*-Phenylphthalimide. *M. Kuhara* and *M. Fukui* 455
Also *α*-compound.

$C_{14}H_{10}O_4N_2$. Oxyphthalylnitrosoaniline. *M. Kuhara* and *M. Fukui* 458
$C_{14}H_{11}ON_3$. Benzoylphenyleneguanidine. *H. L. Wheeler* and *T. B. Johnson* 415
$C_{14}H_{11}O_3N$. Phenylphthalamic acid. *M. Kuhara* and *M. Fukui* 457
$C_{14}H_{12}O_2N_2$. *Sym*-benzoylphenylurea. *R. H. McKee* 228
Also *as*-benzoylphenylurea.

$C_{14}H_{13}ON_3$. Benzoylphenylguanidine. *H. L. Wheeler* and *T. B. Johnson* 417
$C_{14}H_{21}O_{16}O_6$. Styphnic ethyl ether. *C. L. Jackson* and *R. B. Earle* 52
$C_{14}H_{11}NS$. Diphenylmethylisothiocyanate. *H. L. Wheeler* 353
$C_{14}H_{14}NS$. Diphenylmethylthiourea. *H. L. Wheeler* 355

14 IV.

$C_{14}H_{19}ONS_2$. Di-*n*-propylbenzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 195
$C_{14}H_{20}ON_2S$. Benzoyldiethylthioldiethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413

C_{15}-GROUP.

$C_{15}H_{16}S$. Metaxylyl benzyl sulphide. *H. L. Wheeler* and *T. L. Johnson* 205

15 III.

$C_{15}H_{11}O_2N$. Orthotolylphthalimide. *M. Kuhara* and *M. Fukui* 458
s- and *α*-compounds.

$C_{15}H_{12}O_4N_2$. Oxyphthalylnitrosoorthotoluidine. *M. Kuhara* and *M. Fukui* 459
$C_{15}H_{13}O_3N$. Orthotolylphthalamic acid. *M. Kuhara* and *M. Fukui* 459
$C_{15}H_{14}O_2N_2$. Methyl benzoylphenylisourea. *R. H. McKee* 231
Sym. and *as.*-compounds.
$C_{15}H_{15}ON$. Diphenylmethylacetamide. *H. L. Wheeler* 354
$C_{15}H_{15}O_2N_3$. Methyl (*sym.*)-diphenylisobiuret. *R. H. McKee* 233
$C_{15}H_{16}N_2S$. Diphenylmethyl-methylthiourea. *H. L. Wheeler* 355

15 IV.

$C_{15}H_{11}ONS$. Desyl thiocyanate. *H. L. Wheeler* and *T. L. Johnson* 202
$C_{15}H_{12}ON_2S$. Diphenylpseudothiolhydantoïn. *H. L. Wheeler* 353
$C_{15}H_{12}O_3N_2S_2$. Paranitrobenzylbenzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 196
$C_{15}H_{17}O_5NS_2$. Benzoylmetanitrophenylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412
$C_{15}H_{17}O_5NS_2$. Diethyl malonate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* 351

15 V.

$C_{15}H_{12}ONS_2Br$. Parabrombenzyl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 197

C_{16}-GROUP.

$C_{16}H_{10}O_2N_2$. Indigo. *H. Brunck* 387
History of manufacture (Review).

$C_{16}H_{14}O_4N_2$. Diacetyldiamidophenoxozone. *H. W. Hillyer* 364
$C_{16}H_{16}O_2N_2$. Ethyl benzoylphenylisourea. *R. H. McKee* 227
$(C_{16}H_{18}N_2O_3)x$. Bilirubin. *W. R. Orndorff* and *J. E. Teeple* 86
$C_{16}H_{22}N_2S$. Diphenylmethyl-diethylthiourea. *H. L. Wheeler* 355

16 IV.

$C_{16}H_{13}O_3NS_2$. Phenyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 200
$C_{16}H_{15}ONS_2$. Metaxylylbenzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 203
$C_{16}H_{16}ON_2S$. Benzoyl-*p*-tolylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412
$C_{16}H_{29}ON_2S$. Benzoyldipropylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413

16 V.

$C_{16}H_{12}O_{12}N_4Br_2Ba$. Barium salt of bromdinitroethoxyphenol. *C. L. Jackson* and *R. B. Earle* 54

C_{17}-GROUP.

$C_{17}H_{19}O_2N_3$. Ethyl-α-methyl-α-diphenylisobiuret. *R. H. McKee* 239

17 IV.

$C_{17}H_{14}ONS_2$. Mesityl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 205
$C_{17}H_{17}ONS_2$. Ethyl benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 196
$C_{17}H_{18}ON_2S$. Benzoyl-*p*-tolylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414
$C_{17}H_{18}ON_2S$. Benzoylphenylthiolpropylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415
$C_{17}H_{18}O_2N_2S$. Benzoylparaanisylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414

17 V.

$C_{17}H_{17}ON_2ClS$. Benzoyl-*m*-chlorphenylthiol-*n*-propylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415

C_{18}-GROUP.

$C_{18}H_{14}O_6N_2$. Diphenoxydinitrobenzol. *C. L. Jackson* and *W. P. Cohoe* 8
$C_{18}H_{16}ON_4$. Oxyquinonebisphenylhydrazone. *W. R. Orndorff* and *E. D. Thebaud* 162
$C_{18}H_4O_8Br_8$. Ditribrommetoxyphenyldibromorthoquinophenylene ether. *C. L. Jackson* and *W. Koch* 42

18 IV.

$C_{18}H_{14}O_3N_2S_2$. Phthalimidoethyl benzoyldithiocarbamate *H. L. Wheeler* and *T. B. Johnson* 201
$C_{18}H_{17}O_3NS_2$. Ethyl phenyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* 353
$C_{18}H_{20}ON_2S$. Benzoyl-*p*-tolylthiolpropylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415
$C_{18}H_{28}ON_2S$. Benzoyldiisobutylthiolethylpseudothiourea) *H. L. Wheeler* and *T. B. Johnson* 413

18 V.

$C_{18}H_{26}O_2N_4Cl_6Pt$. Ethyl phenylisourea chlorplatinate. *R. H. McKee*. 217

C_{19}-GROUP.

$C_{19}H_{16}$. Triphenylmethane. *J. F. Norris* and *G. MacLeod* 499
On the preparation of.

19 II.

$C_{19}H_{16}O$. Triphenylcarbinol. *J. F. Norris* and *G. MacLeod* 501
$C_{19}H_{15}Cl$. Triphenylchlormethane. *J. F. Norris* and *G. MacLeod* 503

19 III.

$C_{19}H_{14}O_3N_2$. Benzoyldiamidophenoxozone. *H. W. Hillyer* 364
$C_{19}H_{16}C_2N_4$. Resorcindisazobenzene, monomethyl ether of. *W. R. Orndorff* and *E. D. Thebaud* 166

19 IV.

$C_{19}H_{16}ON_2S$. Benzoyl-α-naphthylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412
$C_{19}H_{19}O_3NS_2$. Ethyl acetate derivative of benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 198
$C_{19}H_{19}O_3NS_2$. Ethyl hydrocinnamate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 199
$C_{19}H_{20}O_3NS_2$. Ethyl propionate derivative of benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 201
$C_{19}H_{22}ON_2S$. Benzoylpseudocumylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414

19 V.

$C_{19}H_{18}O_3NS_2Na$. Ethyl hydrocinnamate derivative of sodium benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 199

C_{20}-GROUP.

$C_{20}H_{10}O_6$. Coeruleïn. *W. R. Orndorff* and *C. E. Brewer* 97
Constitution; experimental.
$C_{20}H_{12}O_7$. Galleïn. *W. R. Orndorff* and *C. E. Brewer* 97
Constitution; experimental.
$C_{20}H_{16}O_4$. Phenolphthalin. *J. H. Kastle* and *O. M. Shedd* 526
Reagent for oxidizing ferments.

20 III.

$C_{20}H_{17}ON$. Diphenylmethylbenzamide. *H. L. Wheeler* 354
$C_{20}H_{12}O_{11}Pb_4$. Basic lead salt of galleïn. *W. R. Orndorff* and *C. E. Brewer* 134
$C_{20}H_{18}NS$. Triphenylmethyl thiocyanate. *H. L. Wheeler* 358
$C_{20}H_{18}N_2S$. Diphenylmethyl-phenylthiourea. *H. L. Wheeler* 356
$C_{20}H_{18}N_3S$. Diphenylmethyl-phenylthiosemicarbazide. *H. L. Wheeler* 356

C_{21}-GROUP.

$C_{21}H_{12}O_6$. Monomethyl ethers of coeruleïn. *W. R. Orndorff* and *C. E. Brewer*. 144
$C_{21}H_{14}O_7$. Methyl ester of galleïn. *W. R. Orndorff* and *C. E. Brewer* 130

21 III.

$C_{21}H_{17}O_2N_3$. Dibenzoylphenylguanidine. *R. H. McKee* 222
$C_{21}H_{18}OS$. Triphenylmethyl thiolacetate. *H. L. Wheeler* 357
$C_{21}H_{20}N_2S$. Diphenylmethyl-methylphenylthiourea. *H. L. Wheeler* 356

21 IV.

$C_{21}H_{18}ON_2S$. Benzoylphenylthiolbenzylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 416

C_{22}-GROUP.

$C_{22}H_{14}O_6$. Coeruleïn monomethyl ester. *W. R. Orndorff* and *C. E. Brewer* 145
$C_{22}H_{18}O_7$. Ethyl ester of galleïn. *W. R. Orndorff* and *C. E. Brewer* 131

22 III.

$C_{22}H_{30}N_2S$. Diphenylmethyldiisobutylthiourea. *H. L. Wheeler* 355

22 IV.

$C_{22}H_{18}O_3N_2S_2$. Benzyl paranitrobenzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 197
$C_{22}H_{19}ONS_2$. Dibenzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 196
$C_{22}H_{20}ON_2S$. Benzoyldiphenylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414
$C_{22}H_{20}ON_2S$. Benzoylphenylthiol-*m*-xylylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 417

C_{23}-GROUP.

$C_{23}H_{18}O_7$. Galleïn trimethyl ether. *W. R. Orndorff* and *C. E. Brewer* 134

23 IV.

$C_{23}H_{21}ONS_2$. Benzyl-*m*-xylyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 203

C_{24}-GROUP.

$C_{24}H_{20}O_7$. Galleïn tetramethyl ethers (colored and colorless). *W. R. Orndorff* and *C. E. Brewer* 137

24 III.

$C_{24}H_{19}ON_3$. Dianilinoquinoneanil. *C. L. Jackson* and *W. Koch* 33
$C_{24}H_{19}O_4N_5$. Trianilidodinitrobenzol. *C. L. Jackson* and *G. E. Behr* 61
$C_{24}H_{20}N_2S$. Diphenylmethyl-β-naphthylthiourea. *H. L. Wheeler* 356

24 IV.

$C_{24}H_{23}ONS_2$. Dixylyl benzoylimidodithiocarbonic ester. *H. L. Wheeler* and *T. B. Johnson* 205
$C_{24}H_{23}ONS_2$. Benzyl mesityl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 206

24 V.

$C_{24}H_{22}O_4N_4Cl_6Pt$. Diamidophenoxozonechlorplatinate. *H. W. Hillyer* 363

C_{25}-GROUP.

$C_{25}H_{20}O_8$. Trimethylgalleïn monacetate. *W. R. Orndorff* and *C. E. Brewer* 136
$C_{25}H_{24}O_7$. Galleïn pentamethyl ether. *W. R. Orndorff* and *C. E. Brewer* 141

25 IV.

$C_{25}H_{20}O_3N_2S_2$. Phthalimidoethyl benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 202

C_{26}-GROUP.

$C_{26}H_{16}O_9$. Coeruleïn triacetate. *W. R. Orndorff* and *C. E. Brewer* 142
$C_{26}H_{24}O_7$. Galleïn triethyl ether. *W. R. Orndorff* and *C. E. Brewer* 140

26 III.

$C_{26}H_{20}OS$. Triphenylmethyl thiolbenzoate. *H. L. Wheeler* 357

26 IV.

$C_{26}H_{22}ON_2S$. Benzoyl-*a*-naphthylthiolmetaxylylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 418

C_{28}-GROUP.

$C_{28}H_{20}O_{11}$. Galleïn tetracetate. *W. R. Orndorff* and *C. E. Brewer* 119
$C_{28}H_{22}O_{11}$. Hydrogalleïn tetracetate. *W. R. Orndorff* and *C. E. Brewer* 125
$C_{28}H_{22}O_{11}$. Gallin tetracetate. *W. R. Orndorff* and *C. E. Brewer* 127
Also the silver salt.
$C_{28}H_{22}O_{11}$. Gallol acetate. *W. R. Orndorff* and *C. E. Brewer* 128
$C_{28}H_{28}O_7$. Galleïn tetraethyl ethers (colored and colorless). *W. R. Orndorff* and *C. E. Brewer* 138

28 III.

$C^2{}_8H_{21}O_{11}Ag$. Silver salt of gallin tetracetate. *W. R. Orndorff* and *C. E. Brewer* 130

C_{30}-GROUP.

$C_{80}H_{22}O_{11}$. Coerulin pentacetate. *W. R. Orndorff* and *C. E. Brewer* 143

30 III.

$C_{30}H_2O_{12}N_4$. Dinitroresorcindiphenyl ether. *C. L. Jackson* and *W. P. Cohoe* ... 7

C_{32}-GROUP.

$C_{32}H_{80}O_2N_4S_2$. Diphenylene-di(benzoylthiolethylpseudothiourea). *H. L. Wheeler* and *T. B. Johnson* 415

C_{33}-GROUP.

$C_{33}H_{20}O_8$. Benzoxy-*o*-quino-*o*-dibenzoxydiphenyl. *C. L. Jackson* and *W. Koch*. 27

C_{34}-GROUP.

$C_{34}H_{84}O_4N_4S_2$. Dimethoxydiphenylene-di(benzoylthiolethylpseudothiourea). *H. L. Wheeler* and *T. B. Johnson* 416

C_{41}-GROUP.

$C_{41}H_{27}O_{10}N_3$. Galleïn triphenylcarbamate. *W. R. Orndorff* and *C. E. Brewer*. 132

C_{48}-GROUP.

$C_{48}H_{28}O_{15}$. Galleïn tetrabenzoate. *W. R. Orndorff* and *C. E. Brewer* 124

16 IV.

$C_{16}H_{13}O_3NS_2$. Phenyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 200

$C_{16}H_{15}ONS_2$. Metaxylylbenzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 203

$C_{16}H_{16}ON_2S$. Benzoyl-*p*-tolylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412

$C_{16}H_{29}ON_2S$. Benzoyldipropylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 413

16 V.

$C_{16}H_{12}O_{12}N_4Br_2Ba$. Barium salt of bromdinitroethoxyphenol. *C. L. Jackson* and *R. B. Earle* 54

C_{17}-GROUP.

$C_{17}H_{19}O_2N_3$. Ethyl-α-methyl-α-diphenylisobiuret. *R. H. McKee* 239

17 IV.

$C_{17}H_{14}ONS_2$. Mesityl benzoyldithiocarbamate. *H. L. Wheeler* and *T. B. Johnson* 205

$C_{17}H_{17}ONS_2$. Ethyl benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 196

$C_{17}H_{18}ON_2S$. Benzoyl-*p*-tolylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414

$C_{17}H_{18}ON_2S$. Benzoylphenylthiolpropylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415

$C_{17}H_{18}O_2N_2S$. Benzoylparaanisylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414

17 V.

$C_{17}H_{17}ON_2ClS$. Benzoyl-*m*-chlorphenylthiol-*n*-propylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415

C_{18}-GROUP.

$C_{18}H_{14}O_6N_2$. Diphenoxydinitrobenzol. *C. L. Jackson* and *W. P. Cohoe* 8

$C_{18}H_{16}ON_4$. Oxyquinonebisphenylhydrazone. *W. R. Orndorff* and *E. D. Thebaud* 162

$C_{18}H_4O_6Br_8$. Ditribrommetoxyphenyldibromorthoquinophenylene ether. *C. L. Jackson* and *W. Koch* 42

18 IV.

$C_{18}H_{14}O_3N_2S_2$. Phthalimidoethyl benzoyldithiocarbamate *H. L. Wheeler* and *T. B. Johnson* 201

$C_{18}H_{17}O_3NS_2$. Ethyl phenyl acetate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* 353

$C_{18}H_{20}ON_2S$. Benzoyl-*p*-tolylthiolpropylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 415

$C_{18}H_{28}ON_2S$. Benzoyldiisobutylthiolethylpseudothiourea) *H. L. Wheeler* and *T. B. Johnson* 413

18 V.

$C_{18}H_{26}O_2N_4Cl_6Pt$. Ethyl phenylisourea chlorplatinate. *R. H. McKee.* 217

C_{19}-GROUP.

$C_{19}H_{16}$. Triphenylmethane. *J. F. Norris* and *G. MacLeod* 499
On the preparation of.

19 II.

$C_{19}H_{16}O$. Triphenylcarbinol. *J. F. Norris* and *G. MacLeod* 501
$C_{19}H_{15}Cl$. Triphenylchlormethane. *J. F. Norris* and *G. MacLeod* 503

19 III.

$C_{19}H_{14}O_3N_2$. Benzoyldiamidophenoxozone. *H. W. Hillyer* 364
$C_{19}H_{16}C_2N_4$. Resorcindisazobenzene, monomethyl ether of. *W. R. Orndorff* and *E. D. Thebaud* 166

19 IV.

$C_{19}H_{16}ON_2S$. Benzoyl-α-naphthylthiolmethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 412
$C_{19}H_{19}O_3NS_2$. Ethyl acetate derivative of benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 198
$C_{19}H_{19}O_3NS_2$. Ethyl hydrocinnamate derivative of benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 199
$C_{19}H_{20}O_3NS_2$. Ethyl propionate derivative of benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 201
$C_{19}H_{22}ON_2S$. Benzoylpseudocumylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 414

19 V.

$C_{19}H_{18}O_3NS_2Na$. Ethyl hydrocinnamate derivative of sodium benzoyldithiocarbamic acid. *H. L. Wheeler* and *T. B. Johnson* 199

C_{20}-GROUP.

$C_{20}H_{10}O_6$. Coeruleïn. *W. R. Orndorff* and *C. E. Brewer* 97
Constitution; experimental.

$C_{20}H_{12}O_7$. Galleïn. *W. R. Orndorff* and *C. E. Brewer* 97
Constitution; experimental.

$C_{20}H_{16}O_4$. Phenolphthalin. *J. H. Kastle* and *O. M. Shedd* 526
Reagent for oxidizing ferments.

20 III.

$C_{20}H_{17}ON$. Diphenylmethylbenzamide. *H. L. Wheeler* 354
$C_{20}H_{12}O_{11}Pb_4$. Basic lead salt of galleïn. *W. R. Orndorff* and *C. E. Brewer* 134
$C_{20}H_{18}NS$. Triphenylmethyl thiocyanate. *H. L. Wheeler* 358
$C_{20}H_{18}N_2S$. Diphenylmethyl-phenylthiourea. *H. L. Wheeler* 356
$C_{20}H_{18}N_3S$. Diphenylmethyl-phenylthiosemicarbazide. *H. L. Wheeler* 356

C_{21}-GROUP.

$C_{21}H_{12}O_6$. Monomethyl ethers of coeruleïn. *W. R. Orndorff* and *C. E. Brewer*. 144
$C_{21}H_{14}O_7$. Methyl ester of galleïn. *W. R. Orndorff* and *C. E. Brewer* 130

21 III.

$C_{21}H_{17}O_2N_3$. Dibenzoylphenylguanidine. *R. H. McKee* 222
$C_{21}H_{18}OS$. Triphenylmethyl thiolacetate. *H. L. Wheeler* 357
$C_{21}H_{20}N_2S$. Diphenylmethyl-methylphenylthiourea. *H. L. Wheeler* 356

21 IV.

$C_{21}H_{18}ON_2S$. Benzoylphenylthiolbenzylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson*........ 416

C_{22}-GROUP.

$C_{22}H_{14}O_6$. Coeruleïn monomethyl ester. *W. R. Orndorff* and *C. E. Brewer*.... 145
$C_{22}H_{16}O_7$. Ethyl ester of galleïn. *W. R. Orndorff* and *C. E. Brewer*.... 131

22 III.

$C_{22}H_{30}N_2S$. Diphenylmethyldiisobutylthiourea. *H. L. Wheeler*........ 355

22 IV.

$C_{22}H_{18}O_3N_2S_2$. Benzyl paranitrobenzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson*........ 197
$C_{22}H_{19}ONS_2$. Dibenzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson*........ 196
$C_{22}H_{20}ON_2S$. Benzoyldiphenylthiolethylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson*........ 414
$C_{22}H_{20}ON_2S$. Benzoylphenylthiol-*m*-xylylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson*........ 417

C_{23}-GROUP.

$C_{23}H_{18}O_7$. Galleïn trimethyl ether. *W. R. Orndorff* and *C. E. Brewer*........ 134

23 IV.

$C_{23}H_{21}ONS_2$. Benzyl-*m*-xylyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson*........ 203

C_{24}-GROUP.

$C_{24}H_{20}O_7$. Galleïn tetramethyl ethers (colored and colorless). *W. R. Orndorff* and *C. E. Brewer*........ 137

24 III.

$C_{24}H_{19}ON_3$. Dianilinoquinoneanil. *C. L. Jackson* and *W. Koch*........ 33
$C_{24}H_{19}O_4N_5$. Trianilidodinitrobenzol. *C. L. Jackson* and *G. E. Behr*........ 61
$C_{24}H_{20}N_2S$. Diphenylmethyl-β-naphthylthiourea. *H. L. Wheeler*........ 356

24 IV.

$C_{24}H_{23}ONS_2$. Dixylyl benzoylimidodithiocarbonic ester. *H. L. Wheeler* and *T. B. Johnson*........ 205
$C_{24}H_{23}ONS_2$. Benzyl mesityl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson*........ 206

24 V.

$C_{24}H_{22}O_4N_4Cl_6Pt$. Diamidophenoxozonechlorplatinate. *H. W. Hillyer*........ 363

C_{25}-GROUP.

$C_{25}H_{20}O_8$. Trimethylgalleïn monacetate. *W. R. Orndorff* and *C. E. Brewer*.... 136
$C_{25}H_{24}O_7$. Galleïn pentamethyl ether. *W. R. Orndorff* and *C. E. Brewer*...... 141

25 IV.

$C_{25}H_{20}O_3N_2S_2$. Phthalimidoethyl benzyl benzoylimidodithiocarbonate. *H. L. Wheeler* and *T. B. Johnson* 202

C_{26}-GROUP.

$C_{26}H_{16}O_9$. Coeruleïn triacetate. *W. R. Orndorff* and *C. E. Brewer* 142
$C_{26}H_{24}O_7$. Galleïn triethyl ether. *W. R. Orndorff* and *C. E. Brewer* 140

26 III.

$C_{26}H_{20}OS$. Triphenylmethyl thiolbenzoate. *H. L. Wheeler* 357

26 IV.

$C_{26}H_{22}ON_2S$. Benzoyl-α-naphthylthiolmetaxylylpseudothiourea. *H. L. Wheeler* and *T. B. Johnson* 418

C_{28}-GROUP.

$C_{28}H_{20}O_{11}$. Galleïn tetracetate. *W. R. Orndorff* and *C. E. Brewer* 119
$C_{28}H_{22}O_{11}$. Hydrogalleïn tetracetate. *W. R. Orndorff* and *C. E. Brewer* 125
$C_{28}H_{22}O_{11}$. Gallin tetracetate. *W. R. Orndorff* and *C. E. Brewer* 127
Also the silver salt.
$C_{28}H_{22}O_{11}$. Gallol acetate. *W. R. Orndorff* and *C. E. Brewer* 128
$C_{28}H_{28}O_7$. Galleïn tetraethyl ethers (colored and colorless). *W. R. Orndorff* and *C. E. Brewer* 138

28 III.

$C^2{}_8H_{21}O_{11}Ag$. Silver salt of gallin tetracetate. *W. R. Orndorff* and *C. E. Brewer* 130

C_{30}-GROUP.

$C_{30}H_{22}O_{11}$. Coerulin pentacetate. *W. R. Orndorff* and *C. E. Brewer* 143

30 III.

$C_{30}H_2O_{12}N_4$. Dinitroresorcindiphenyl ether. *C. L. Jackson* and *W. P. Cohoe* ... 7

C_{32}-GROUP.

$C_{32}H_{30}O_2N_4S_2$. Diphenylene-di(benzoylthiolethylpseudothiourea). *H. L. Wheeler* and *T. B. Johnson* 415

C_{33}-GROUP.

$C_{33}H_{20}O_8$. Benzoxy-*o*-quino-*o*-dibenzoxydiphenyl. *C. L. Jackson* and *W. Koch*. 27

C_{34}-GROUP.

$C_{34}H_{34}O_4N_4S_2$. Dimethoxydiphenylene-di(benzoylthiolethylpseudothiourea). *H. L. Wheeler* and *T. B. Johnson* 416

C_{41}-GROUP.

$C_{41}H_{27}O_{10}N_3$. Galleïn triphenylcarbamate. *W. R. Orndorff* and *C. E. Brewer*. 132

C_{48}-GROUP.

$C_{48}H_{28}O_{15}$. Galleïn tetrabenzoate. *W. R. Orndorff* and *C. E. Brewer* 124

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